

IV. SORPTION AND SORPTION MODELING STUDIES

A. BATCH-SORPTION DATA

Introduction

The solubility limits of radionuclides can act as an initial barrier to radionuclide migration from the potential repository at Yucca Mountain. However, once radionuclides have dissolved in water infiltrating the site, sorption of these radionuclides onto the surrounding tuffs becomes a potentially important second barrier. Thus, the study of the retardation of actinides and other key radionuclides is of major importance in assessing the performance of the potential repository.

Sorption actually comprises several physicochemical processes, including ion exchange, adsorption, and chemisorption. Determining whether sorption will occur requires knowledge of the likely flow paths of the groundwater and the spatial and temporal distribution of sorbing minerals along these paths. Evaluating the retardation effectiveness of sorption for repository design and licensing requires theoretical and quantitative understanding of sorption. We thus combined experimental measurements of sorption with modeling of the data in an attempt to identify key sorption mechanisms.

The use of batch-sorption experiments to obtain sorption distribution coefficients and to identify sorption mechanisms is fast, easy, and inexpensive compared to other types of sorption experiments. A disadvantage is the fact that such experiments are static in nature, whereas transport of radionuclides through the site is, obviously, a dynamic process. However, batch-sorption experiments are useful for bounding more detailed and mechanistic sorption studies, and a major part of our experimental effort was devoted to such measurements.

In our experiments, we determined batch-sorption distribution coefficients as a function of variables representing conditions expected beyond the region disturbed by waste emplacement. The variables

included mineralogy, groundwater chemistry, sorbing element concentration, atmospheric conditions, and temperature. Batch-sorption results are very sample specific and, therefore, difficult to generalize and apply throughout the mountain. Deconvolution of sorption isotherms provides much greater detail about sorption sites (kind, number, specificity, and so forth), and we did this analysis for a number of the actinides. Such information is correlated with crystallographic data and related to specific sorption sites in the crystal structure. All sites are not equally selective for all sorbing species.

We also examined the sorption behavior of individual pure minerals, such as the zeolites and manganese or iron oxyhydroxides found in Yucca Mountain tuffs. This approach can help predict sorption coefficients along flow paths of known mineral content.

Linear versus nonlinear sorption

The sorption distribution coefficient, K_d , for the species being sorbed, is the ratio of its concentration in the solid phase, F , to its concentration in the solution phase, C , which implies a linear relationship between the concentrations:

$$F = K_d C \quad (12)$$

Besides linearity, the valid use of sorption distribution coefficients in transport calculations also requires the sorption to be instantaneous and reversible, conditions that may or may not be met for the sorption of radionuclides onto Yucca Mountain tuffs.

Nonlinear adsorption isotherms have been reviewed by de Marsily (1986, p. 258). A useful nonlinear relationship, Freundlich's isotherm, is given by the equation

$$F = K C^{1/n} \quad (13)$$

where K and n are positive constants (with $n \geq 1$). Another nonlinear relationship is Langmuir's

isotherm, given by

$$F = \frac{K_1 C}{1 + K_2 C}, \quad (14)$$

where K_1 and K_2 are positive constants. Part of our research was an attempt to assess the validity of using the linear distribution coefficients as opposed to other isotherm functional forms to describe retardation by sorption in transport calculations.

Mechanistic models

A better understanding of the sorption of radionuclides onto tuff is possible if we can relate the data to mechanistic models. Two general mechanisms are important: ion-exchange reactions that are primarily electrostatic in nature and surface complexation in which a relatively covalent chemical bond forms with the mineral surface. Ion exchange does not have the same degree of selectivity between aqueous ions of like charge as does surface complexation. The adsorption of metal ions via cation exchange will only occur on surfaces of opposite charge and so is affected by such common components of groundwater as sodium. Surface complexation, on the other hand, can occur even when the mineral surface charge is the same as the aqueous ion. Both of these processes can, in principle, be modeled using a triple-layer surface-complexation model. However, there are significant differences between the cation exchange in zeolites and clays and the formation of surface complexes on metal oxides, so we have treated cation exchange and surface complexation separately.

Physiochemical processes that might accelerate radionuclide migration relative to groundwater flow rates must also be quantified. For example, mineral surfaces in rock pores are predominantly negatively charged, so anions are typically repelled and can actually migrate through the rock faster even than the water. Such acceleration processes depend largely on the molecular complexation or speciation that occurs in solution. Accordingly, detailed assessment of this possibility is needed to fully evaluate the potential for transport retardation by geochemical processes.

Experimental procedures

All batch-sorption experiments were performed at room temperature. The procedure first involved pretreating the solid phase with the groundwater being studied (J-13 or UE-25 p#1 well water or a synthetic bicarbonate groundwater) in the ratio of 1 g of solid to 20 ml of solution. The pretreated solid phase was then separated from the groundwater by centrifugation and equilibrated with 20 ml of a radionuclide solution (in the groundwater being studied). After sorption, the phases were again separated by centrifugation.

The amount of radionuclide in solution initially and then after sorption was either determined with a liquid-scintillation counter (such as for neptunium and plutonium) or with inductively coupled plasma mass spectrometry (such as for uranium). The amount of radionuclide in the solid phase was determined by difference.

The liquid-scintillation counting technique we used can discriminate alpha activity from beta activity. Consequently, no interference from beta emitters (such as ^{233}Pa , the daughter of ^{237}Np) is expected. Because the efficiency of this liquid-scintillation counter is approximately 100%, the counts per minute (cpm) measured are approximately equivalent to disintegrations per minute.

As controls, we used container tubes without solid phases in them to monitor radionuclide precipitation and sorption onto the container walls during the sorption experiment. The difference in the concentration of the radionuclide in the initial solution and in the solution in the control tube generally was only a few percent, and then in either a plus or a minus direction.

Results for the plutonium solution did show a small amount of sorption onto the container walls. Even here, the difference in concentration between the initial plutonium solution and the plutonium solution in the control tube never exceeded 7% for the experiments reported. Nevertheless, in the case of plutonium, we calculated the amount of radionu-

clide sorbed in the solid phase by taking the difference of the final plutonium solution concentration both with the initial solution concentration and with the solution concentration in the control tube. The latter approach is conservative because plutonium may sorb to container walls only in the absence of the geologic material.

We performed batch-sorption experiments under atmospheric conditions and inside glove boxes with a carbon-dioxide overpressure. The pH of the J-13 and UE-25 p#1 waters under atmospheric conditions was approximately 8.5 and 9, respectively, and inside the glove boxes was 7 (the carbon-dioxide overpressure was adjusted to bring the pH of both waters down to 7). Details of the experimental setup and the analytical techniques that we used in the sorption experiments are given in the *Yucca Mountain Project Detailed Procedures* (Table 2).

The distribution coefficient

The batch-sorption distribution coefficient, K_d , was calculated using

$$K_d = \frac{F}{C} = \frac{\text{moles of radionuclide per g of solid phase}}{\text{moles of radionuclide per ml of solution}} \quad (15)$$

K_d thus has units of ml/g.

Determination of very small or very large batch-sorption distribution coefficients results in large uncertainties in the K_d values calculated. When very little sorption occurs, calculations can yield negative K_d values; the error results from subtracting two large numbers (the initial radionuclide concentration in solution and the radionuclide concentration after sorption) to obtain a small number (the amount of radionuclide left in the solid phase).

Therefore, small K_d values (in the range of ± 1) are not significant. On the other hand, when a great deal of sorption occurs, calculations can yield large uncertainties associated with measuring the small amount of radioactivity left in solution after sorption. Because of these uncertainties, most K_d values are only reported to one significant figure.

Niobium, Thorium, Tin, and Zirconium

The radionuclides of concern represented by these elements have several characteristics in common. First, in groundwater-rock systems of concern in this report, these elements have stable oxidation states. Niobium is present in a +5 oxidation state, whereas the others are typically in +4 oxidation states (Brookins 1988). Second, in aqueous solutions with compositions typical of groundwaters, these elements tend to occur as sparingly soluble oxides or silicates (Brookins 1988). They may also form solid solutions with other, more common, sparingly soluble oxides, such as titania (TiO_2). Third, the dominant solution species associated with these oxides are hydrolysis products (Baes and Mesmer 1976). Fourth, the hydrolyzed solution species tend to have high affinities for adsorption onto oxide surfaces as discussed further below. The radionuclides represented by these elements are in the “strongly-sorbing” group discussed by Meijer (1992).

Niobium

Behavior in solutions representative of Yucca Mountain groundwaters.

According to Baes and Mesmer (1976), at a dissolved niobium concentration of 10^{-6} M, the dominant solution species in pure water are the neutral species $\text{Nb}(\text{OH})_5$ and the anionic species $\text{Nb}(\text{OH})_6^-$. The anionic species predominates at values of pH above 7, and the neutral species is stable below a pH of 7. At surficial temperatures and pressures, evidence for significant complexation of niobium by nonhydroxide ligands in natural aqueous solutions is lacking. As discussed below, carbonate complexation may occur at higher temperatures and pressures.

The concentrations of niobium in surficial aqueous solutions are extremely low, presumably due to the low solubility of the pentavalent oxide (Baes and Mesmer 1976) and to sorption onto mineral surfaces. In geologic systems, niobium may substitute as a trace element in the more abundant oxide phases such as micas, titanium oxides (for exam-

ple, rutile), and clays (Goldschmidt 1958). This effect also leads to low solution concentrations.

Qualitative evidence for behavior in the surficial environment.

The geologic literature contains numerous papers that qualitatively discuss the mobility, or more accurately, the immobility of niobium in rocks during alteration processes (for example, Cann 1970). In various studies of soils or altered, weathered, or metamorphosed rocks, geological, geochemical, and statistical evidence has been presented that supports the conclusion that niobium is essentially immobile in the surficial environment. Although some of these studies deal with rocks that have been altered under conditions of low fluid-to-rock ratios, the general lack of evidence for niobium mobility suggests that this element would also be immobile in systems with higher water-rock ratios, such as the Yucca Mountain flow system. For example, Brookins (1983) notes that 100 per cent of the niobium produced by fission at the natural reactor at Oklo, Gabon, has been retained by the host pitchblende even though the reactor was active in water-bearing sandstones that were subjected to elevated temperatures during and after the critical (that is, nuclear) stage of the reactor.

Grimaldi and Berger (1961) studied the concentrations of niobium in twenty lateritic soils from West Africa and concluded that silica is depleted more rapidly from these soils than is niobium and niobium more rapidly than aluminum. Further, these workers note that there is a strong association of niobium with the clay-sized fraction and also with titanium. They propose that the association of niobium with the clay fraction may be due to the presence of niobium-rich authigenic rutile in the clays. The observation that niobium was mobilized more readily than aluminum in this environment does not necessarily imply niobium was transported out of the system as a dissolved solution species. The tendency of elements such as niobium, titanium, tin, and so forth to form very fine-grained precipitates is well known. Such colloidal-sized particles can be transported by soil solutions and surface waters.

Evidence for niobium mobility during greenschist metamorphism of mafic rocks has been presented by Murphy and Hynes (1986). These workers suggest that carbonate-rich metamorphic solutions can mobilize and transport niobium (as well as titanium, zirconium, phosphorus, and yttrium).

Presumably, carbonate can form mobile complexes with niobium under conditions of elevated temperature and pressure. No references were found that address the ability of carbonate to complex niobium under low temperatures and near atmospheric pressures.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

On the basis of the geological evidence and because niobium forms primarily hydrolyzed species in groundwaters of the type associated with Yucca Mountain, niobium should be very insoluble in Yucca Mountain groundwaters and strongly sorbed onto mineral phases present in Yucca Mountain tuffs from the whole range of groundwater compositions expected at the site.

Thorium

Behavior in solutions representative of Yucca Mountain groundwaters.

Langmuir and Herman (1980) have compiled and critically reviewed thermodynamic data for thirty-two dissolved thorium species and nine thorium-bearing solid phases. In the groundwater compositions expected within Yucca Mountain, thorium will be fully hydrolyzed ($\text{Th}(\text{OH})_4$), and thorium complexing with other inorganic ligands will be insignificant based on the data presented in Langmuir and Herman (1980). Thorium compounds are among the most insoluble in the group of elements considered in this report. Solubilities in the range of 10^{-50} M are common for thorium compounds (for example, thorianite (ThO_2) and thorite (ThSiO_4)). Nevertheless, concentrations well above this range have been found in various natural waters and appear to reflect complexation with organic ligands in organic-rich waters. Such waters are not expected at Yucca Mountain.

Qualitative evidence for behavior in the surficial environment.

Thorium is one of the elements considered to be immobile in most surficial environments (Rose et al. 1979). Studies of the isotopic disequilibrium in the uranium and thorium decay series found in natural aquifers suggest that thorium isotopes are strongly retarded in these flow systems relative to other members of the decay series (Krishnaswami et al. 1982). Studies of the migration of thorium away from thorium ore bodies also indicate that it is "extraordinarily immobile" in these environments (Eisenbud et al. 1984). Brookins (1983) found that thorium was immobile in the Oklo reactor environment. Studies of thorium concentration gradients with depth in seawater also point to high sorption affinities for this element on oceanic particulate matter (Moore and Hunter 1985).

Data from laboratory sorption experiments.

Hunter et al. (1988) carried out thorium sorption experiments on MnO_2 and FeOOH in artificial seawater and in a simple NaCl solution. The primary objective was to determine the effects of major ions (for example, Mg^{2+} and SO_4^{2-}) on the adsorption of thorium by goethite (FeOOH) and MnO_2 relative to sorption in a pure NaCl electrolyte system. The effects of magnesium and calcium ions on thorium adsorption were very small (probably within the margin of experimental error), but the presence of sulfate at seawater concentrations (0.028 M) increased the adsorption edge on FeOOH by one-half of a pH unit. Because the adsorption edge is in the range of pH values from 3 to 5 in all the experiments, this effect is not considered important for thorium sorption behavior at the Yucca Mountain site.

LaFlamme and Murray (1987) evaluated the effects of carbonate on the adsorption characteristics of thorium on goethite. They found that carbonate alkalinity could decrease thorium sorption onto goethite at alkalinity values greater than 100 meq/l. Because the alkalinity values expected in the Yucca Mountain flow system are orders of magnitude lower than this value, carbonate alkalinity

is not expected to affect thorium adsorption behavior in this system.

According to Langmuir and Herman (1980), the adsorption of thorium onto clays, oxides, and organic material increases with pH and approaches 100 per cent completion by a pH of about 6.5. As the thorium ion is largely hydrolyzed above a pH of about 3.2, it follows that hydroxy complexes of thorium are primarily involved in adsorption processes (in carbonate-poor systems). Using a mixed quartz-illite soil as a sorbent, Rancon (1973) measured a K_d value of 5 ml/g at a pH of 2, which increased to 5×10^5 ml/g at a pH of 6. With a quartz-illite-calcite-organic-matter soil, Rancon found that the K_d decreased from 10^6 ml/g at a pH of 8 to 100 ml/g at a pH of 10. This change was attributed to the dissolution of soil humic acids and the formation of thorium-organic complexes at this high pH.

Lieser and Hill (1991) reported thorium sorption coefficients for rock-water systems associated with the Gorleben site in Germany. They found that thorium was strongly sorbed in such systems ($K_d = 10^3$ – 10^5 ml/g). However, they also found that colloidal transport may be of potential significance to the migration of thorium in the surficial environment.

Thorium sorption experiments on Yucca Mountain rock samples in J-13 groundwater were reported by Rundberg et al. (1985) and Thomas (1988). The sorption coefficients obtained in these experiments ranged from 140 to 23,800 ml/g. No correlations were noted between the values obtained for the sorption coefficient and rock type or pH (5.3–7.5). Part of the reason for the large range in sorption coefficients obtained in these experiments may lie in the presence of fine colloidal particles in the solution phase used to obtain the sorption coefficients (for example, Lieser and Hill 1991).

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The dominance of hydrolysis reactions in solution,

the low solubility of thorium oxides and silicates, the large values measured for thorium sorption coefficients in different water compositions, including seawater, combined with the general lack of evidence for mobility of thorium in the surficial environment suggest that the sorption coefficients for thorium will be large (> 100 mg/l) in all hydrochemical environments associated with Yucca Mountain in the present day or in the future.

Tin

Behavior in solutions representative of Yucca Mountain groundwaters.

The dominant tin solution species in surficial waters appears to be $\text{Sn}(\text{OH})_4$. The concentrations of tin in natural groundwaters are extremely low due to the low solubility of the tetravalent oxides (about 10^{-9} M in pure water; Baes and Mesmer 1976). Cassiterite (SnO_2) should be the solubility-limiting oxide in most groundwaters. Tin could also coprecipitate with other insoluble oxides or silicates such as niobium pentoxide, zirconium and thorium dioxide, and thorium silicate. In natural waters with high sulfide concentrations, tin sulfide minerals could control tin solubility. However, such water compositions are not expected in association with the proposed repository site at Yucca Mountain.

Qualitative evidence for behavior in the surficial environment.

Tin is one of the elements considered to be immobile in most near-surface geologic environments (Rose et al. 1979). This assignment is based on various types of data, including observations on the mobility of tin in and around tin ore deposits.

However, De Laeter et al. (1980) note that some tin has migrated out of the pitchblende at the natural reactor at Oklo, Gabon. The cause for this migration has not been established but may reflect the existence of reducing conditions during some phase of the history of the reactor.

Data from laboratory sorption experiments.

Sorption experiments with tin have been carried out on several whole-rock samples from Yucca

Mountain in contact with J-13 water, UE-25 p#1 water, H-3 water, and several waters separately spiked with sodium sulfate, sodium bicarbonate, and calcium chloride (Knight and Thomas 1987). The measured sorption coefficients ranged from 77 to 35,800 mg/l at pH values in the range of 8.4 to 9.2. Coefficients obtained from desorption experiments were generally larger (300–52,500 mg/l) than those obtained from sorption experiments. The devitrified tuff samples produced the highest sorption and desorption coefficient values (> 2900 mg/l), whereas the vitric and zeolitic tuff samples produced lower values. Sorption coefficients were generally highest in the UE-25 p#1 water and the calcium-chloride-spiked J-13 water. Apparently, high calcium concentrations in the solution phase result in high sorption-coefficient values for tin. Alternatively, high calcium concentrations cause the precipitation of some type of tin-bearing compound. As with thorium, the large range in sorption coefficients observed in the experiments may reflect the presence of colloidal-size particles in the solution phase used to obtain the coefficients.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The dominance of hydrolysis reactions in solution, the low solubility of tin oxides, and the large values measured for tin sorption coefficients in different water compositions combined with the general lack of evidence for mobility of tin in the surficial environment suggest that the sorption coefficients for tin will be large (> 100 mg/l) in all hydrochemical environments associated with Yucca Mountain in the present-day or in the future.

Zirconium

Behavior in solutions representative of Yucca Mountain groundwaters.

In near-neutral solutions, the dominant zirconium solution species appear to be hydrolysis products, such as $\text{Zr}(\text{OH})_4$. The degree to which zirconium forms complexes with other inorganic ligands present in Yucca Mountain groundwaters is insignificant (Sillen and Martell 1964, 1971). The solubility of zirconium in dilute solutions is extremely

small ($K_{50} \cong -50$; Sillen and Martell 1964, 1971), although the identity of the solubility-controlling solid is uncertain. The solubility-controlling compounds for zirconium in most natural groundwaters are likely zircon (ZrSiO_4) or baddeleyite (ZrO_2). Zirconium solubilities in surficial environments may also reflect coprecipitation in other sparingly soluble oxides or silicates. The concentrations of zirconium in natural waters may be dominantly controlled by sorption reactions.

Qualitative evidence for behavior in the surficial environment.

Zirconium is one of the elements considered to be immobile in most near-surface geologic environments (Rose et al. 1979). Studies of zirconium concentrations in altered and unaltered or less-altered rocks from the same original geologic unit (Cann 1970) form part of the basis for this conclusion. Other evidence includes the persistence of zircon (ZrSiO_4) in the weathering zone and the low concentrations of zirconium in waters associated with zirconium-rich rocks. Brookins (1983) noted that zirconium was retained within the reactor zones at Oklo, Gabon, although it may have been subject to very local-scale redistribution.

Data from laboratory sorption experiments.

Data on the sorption behavior of zirconium in soil-rock-water systems have been reported by Rhodes (1957), Spitsyn et al. (1956), Prout (1959), Serne and Relyea (1983), and others. Rhodes (1957) has presented data on zirconium sorption coefficients for a soil-water system that show large values ($> 1980 \text{ mg/l}$) up to a pH of 8.0 followed by a decrease to 90 mg/l at a pH of 9.6 and a return to high values at a pH of 12. He attributed the decreased sorption for values of pH from 8 to 12 to the stabilization of colloidal components in solution in this pH range. Spitsyn et al. (1956) observed little movement of zirconium through a sandy soil in a field test under both acidic and alkaline conditions. Serne and Relyea (1983) report large values for zirconium sorption coefficients in all media tested.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The dominance of zirconium hydrolysis reactions in solution suggests that pH will be the dominant groundwater compositional parameter controlling zirconium solubility and sorption behavior. The lack of evidence for zirconium transport in field tests under both acidic and alkaline conditions and the general lack of evidence for mobility of zirconium in the surficial environment combined with the large values of the sorption coefficient reported in the literature for zirconium suggest that in all hydrochemical environments associated with Yucca Mountain in the present-day or in the future this element's sorption coefficients will be large ($> 100 \text{ mg/l}$).

Actinium, Americium, and Samarium

The radionuclides of concern represented by these elements have the following characteristics in common: 1) In groundwater-rock systems of concern in this report, these elements are all present in the +3 oxidation state. 2) In aqueous solutions with compositions typical of groundwaters, the solubility of these elements tends to be controlled by sparingly soluble carbonates, phosphates, fluoride-carbonate complexes, and to a lesser extent, hydroxy-carbonate compounds (Mariano 1989). The elements may also form solid solutions with carbonates, phosphates, fluorides, and oxides of the major cations in groundwaters. 3) The dominant solution species associated with these elements are generally complexes with carbonate, phosphate, and hydroxide ligands (Sillen and Martell 1964, 1971). 4) The solution species tend to have high affinities for adsorption onto oxide surfaces as discussed further below. The radionuclides represented by these elements are all in the "strongly-sorbing" group discussed by Meijer (1992).

Because the chemistry of all three of these elements is similar in aqueous solution and sorption reactions, they will be discussed as a group.

Behavior in solutions representative of Yucca Mountain groundwaters.

The trivalent ions of the rare-earth elements are essentially spherical and form aqueous complexes that are similar to those formed by the alkaline and alkaline-earth elements. Thompson (1979) notes that the partially filled f orbital is so effectively shielded from most chemical bonding that the crystal-field effects are about 100 cm^{-1} compared to values of around $30,000\text{ cm}^{-1}$ for many first-row transition elements. Chemical interactions of the rare-earth elements are almost entirely ionic and the rare-earth elements are not easily polarized owing to their relatively large charge-to-ionic-radius ratio. As noted by Cotton and Wilkinson (1988), the trivalent actinides show many similarities in solution chemistry to the lanthanides. In fact, Nitsche et al. (1994) have used neodymium as a direct analog for americium in solubility studies.

In solution, americium and the rare-earth elements occur as simple (trivalent) cations, carbonate complexes, phosphate complexes, and hydrolysis products (Wood 1990). Complexes with other inorganic ligands (for example, Cl^- , F^- , and SO_4^{2-}) will not be of importance in the water compositions expected in the Yucca Mountain flow system.

Therefore, speciation models for the rare-earth elements and trivalent actinides should consider pH, carbonate-ion concentration, and possibly phosphate-ion concentration as key variables.

According to Byrne and Kim (1993), phosphate complexes will not be significant unless the ratio of the total phosphate concentration to the total carbonate concentration is greater than 1.3×10^{-3} . This condition makes it unlikely that phosphate rare earths or americium complexes will be important in Yucca Mountain groundwaters. Therefore, carbonate complexes are expected to dominate the solution species for these elements. The solubility-controlling solids in Yucca Mountain groundwaters will likely be carbonates, hydroxycarbonates (Kerrisk 1984b), and possibly phosphates (see the following section).

According to Nitsche et al. (1992, 1994), the solu-

bilities of americium compounds in solutions representative of water compositions expected within Yucca Mountain are approximately $1\text{ to }2 \times 10^{-9}\text{ M}$ in J-13 water and $3\text{ to }30 \times 10^{-7}\text{ M}$ in UE-25 p#1 water as a function of pH at 25°C . At 60°C , the solubilities of americium compounds were $1 \times 10^{-8}\text{ to }2.5 \times 10^{-6}\text{ M}$ in J-13 water and $7 \times 10^{-10}\text{ to }3 \times 10^{-9}\text{ M}$ in UE-25 p#1 water as a function of pH. The solubility-controlling solids were found to be hexagonal and orthorhombic forms of AmOHCO_3 . The speciation of americium in these solutions could not be determined due to the low solubilities of americium in these water compositions relative to the detection limits of the available spectroscopic techniques. Preliminary modeling calculations with the speciation code EQ3 suggest that carbonate complexes dominate in both J-13 and UE-25 p#1 waters at 25° and 60°C (Meijer, unpublished).

Qualitative evidence for behavior in the surficial environment.

Although the geological community generally regards the rare-earth elements as immobile during most water-rock alteration processes (Taylor and McLennan 1988), detailed studies of weathering profiles suggest that these elements may be redistributed within these profiles during weathering. Duddy (1980) studied a weathering profile formed on a homogeneous sedimentary rock unit in southeastern Australia. This profile was formed in a cool temperate climate with 200 cm/yr precipitation. The profile contained bleached zones and ferruginous zones in which iron was reduced or oxidized, respectively. The rare-earth elements were up to 7 times enriched in the bleached portions of the profile. Based on the sorption data discussed in the following section, this is somewhat puzzling as one might expect these elements to be coprecipitated or adsorbed to the secondary ferric oxides formed in the profile. In fact, the rare-earth elements appeared to be enriched in vermiculite, an expanding magnesium-ferrous iron trioctahedral clay that formed in the weathering profile as a result of the alteration of biotite. Up to 10 weight per cent of rare-earth elements was reported in ver-

miculites on the basis of electron-probe analyses. The elements originated from the dissolution of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$) and other minerals present higher in the profile.

Banfield and Eggleton (1989) studied the rare-earth elements in an Australian weathering profile formed on granite. These authors also noted that these elements were mobile in the profile. However, they found that (primary) biotite crystals in the granite contained rare-earth-element-rich apatite inclusions or cavities resulting from the dissolution of apatite. The apatite crystals were apparently dissolved during weathering leaving behind fine-grained ($< 10 \text{ CLm}$) rare-earth-element phosphate phases including florencite, rhabdophane ($\text{CePO}_4 \cdot \text{H}_2\text{O}$), and an unidentified phosphate-free aluminum-rare-earth-element mineral, possibly a carbonate, hydroxycarbonate, or fluorocarbonate. Vermiculites were also present in this profile, but they were not analyzed for rare-earth-element contents.

These two studies clearly indicate that the rare-earth elements can be mobilized in the surficial environment. However, they also suggest that this mobilization is generally of a local nature resulting in the precipitation of new rare-earth-element phases or the incorporation of these elements in other secondary phases, such as clays. These studies did not address the question of whether adsorption of the rare-earth elements onto the surfaces of other mineral phases is a significant process in controlling the mobility of these elements in surficial environments. Loubet and Allegre (1977) noted that the light rare-earth elements were not mobilized in the reactor zones at Oklo, Gabon.

Data on the behavior of americium in the surficial environment is limited to anthropogenic examples. Americium was found to be very immobile in most of the studies located in the literature (for example, Means et al. 1978; Carpenter et al. 1987). The main uncertainty regarding the surficial behavior of americium appears to be the degree to which it is mobilized through colloidal transport (for

example, Penrose et al. 1990).

Data from laboratory sorption experiments.

Ion-exchange studies involving the sorption of lanthanide ions on montmorillonitic clays have been reported by Frysinger and Thomas (1960), Aagard (1974), Bruque et al. (1980), and Bonnot-Courtois and Jaffiezic-Renault (1982). These studies conclude that essentially all of the exchange capacity of the clays is available to lanthanide ions and that the exchange reactions are rapid (that is, minutes). Frysinger and Thomas noted that the $\text{Cs}^+ - \text{Y}^{3+}$ binary exchange was not dependent on pH over the range from 3 to 7. At low cesium concentrations, such as are likely to occur in the potential repository horizon, the clay showed a slight preference for the lanthanide ions relative to cesium, and this preference increased with temperature ($30\text{--}75^\circ\text{C}$).

Bruque et al. (1980) only studied the exchange of lanthanide ions with hydrogen-montmorillonite, which is not of interest in this report. However, Bonnot-Courtois and Jaffiezic-Renault (1982) studied the exchange reactions in potassium-, sodium- and calcium-exchanged clays, which are of interest. In the latter study, the rare-earth elements, at initial solution concentrations of 10^{-2} to 10^{-4} M , showed distribution coefficients greater than 1.0 only when the concentrations of the major cations, in the case of sodium and potassium, were below 0.1 M and, in the case of calcium, were below 0.01 M. The rare-earth elements were apparently, to a large degree, sorbed irreversibly, as they could not be readily desorbed from the clay.

Koeppenkastrop and De Carlo (1992, 1993) have evaluated the sorption of the rare-earth elements by iron oxides, manganese oxides, and apatite from high ionic-strength aqueous solutions (that is, ultraviolet-irradiated natural seawater). One nanomole of each rare-earth-element radiotracer was equilibrated with approximately 10 mg of the solid phase in 1 kg of seawater. The pH of the system was maintained at 7.8 in all the experiments. The percentage of rare-earth element adsorbed on FeOOH and MnO_2 was measured in the presence and

absence of carbonate. Carbonate appeared to affect the kinetics of the adsorption reactions but not the extent of adsorption at equilibrium. The sorption reactions equilibrated within tens of minutes.

Under the conditions of the experiments, the rare-earth elements are shown to have very high affinities for the oxide and phosphate phases ($K_d \gg 1,000$ ml/g). Koeppenkastrop and De Carlo (1993) further state that modeling of sorption data derived from experiments with natural particles indicates that desorption rate constants are much smaller than adsorption rate constants.

The high affinity of the rare-earth elements for iron and manganese-oxide phases suggests that these phases would act as “getters” for these elements in surficial environments. Yet the data reported by Duddy (1980) suggest that the rare-earth elements in the weathering profile he studied were preferentially incorporated in vermiculite in the “bleached” zones and not adsorbed onto ferric oxides in the ferruginous zones. This effect suggests that there were other constituents in the solution phase of the profile investigated by Duddy (1980) that had higher affinities for the oxide surfaces than the rare-earth elements and that they were present in sufficient quantity to saturate the available surface sites. A possible candidate would be the Al^{3+} ion (for example, see Brown et al. 1956).

Stammose and Dolo (1990) reported on batch-sorption experiments with americium (10^{-8} M) on clay as a function of pH and ionic strength. The clay used in the experiments was a mixture of kaolinite (7%) and a mixed-layer clay (53% kaolinite/47% smectite). At ionic strengths of 0.01 and 0.1 M ($NaClO_4$), the americium sorption coefficient was greater than 10^3 mg/l over the entire pH range (3–10) addressed by the experiments. In the higher ionic-strength solutions (1 and 3 M), the sorption coefficients were low (10 mg/l) at a pH of 2 but increased to values in the range of 10^4 to 10^5 mg/l for pH values greater than 6.

Overall, the data presented by these authors suggest: 1) the ion-exchange sites on the clay have a

very high selectivity for americium at trace concentrations; 2) sodium ions at sufficiently high concentrations can displace the americium from these sites; 3) americium is also adsorbed in surface-complexation reactions; 4) the surface-complexation reactions define a sorption edge that has minimum values at low pH and reaches a maximum at a pH of approximately 7; 5) americium is adsorbed as an inner-sphere complex, and its adsorption affinity in surface-complexation reactions is therefore not a function of ionic strength; and 6) at trace americium concentrations, carbonate complexation of americium may compete with surface-complexation reactions in the pH range from 8 to 10, leading to a slight decrease in adsorption in this range.

Allard and Beall (1979) have presented americium sorption-coefficient data for a range of mineral types including clays, feldspars, carbonates, phosphates, oxides, oxyhydroxides, and other less common minerals. The sorption coefficients were measured over a range of pH from 4 to 9 in a low ionic-strength (synthetic) groundwater similar in composition to an average Yucca Mountain groundwater. Initial americium solution concentrations were in the range from 1.8 to 5.0×10^{-9} M. Data presented for clay minerals indicate that ion exchange occurred on these minerals in the lower pH range (< 6). Surface recrystallization reactions are evident in the low pH data for apatite (also, see Jonasson et al. 1985) and fluorite. On the remaining silicates and nonsilicates, americium appears to sorb dominantly by surface-complexation reactions. In all cases, the sorption coefficient values are in excess of 10^3 mg/l over the pH range likely to be encountered in the Yucca Mountain groundwaters.

In summary, trivalent actinium, americium, and samarium likely sorb by at least two distinct mechanisms. At pH values less than approximately 6, ion-exchange reactions on clays and other ion-exchanging minerals may dominate the adsorption behavior of these elements in low ionic-strength solutions. These reactions will show dependencies

on ionic strength and ion selectivity. At pH values greater than 6, sorption appears to involve primarily inner-sphere surface-complexation reactions. Although these reactions are independent of ionic strength, they will likely be subject to competition with other sorbing species at sufficiently high sorption densities. In the pH range from 8 to 10, carbonate-complexation reactions in solution may compete with the surface-complexation reactions involving these elements. However, the surface-complexation reactions are expected to dominate over carbonate-complexation reactions in Yucca Mountain groundwaters.

Sorption data obtained on Yucca Mountain samples.

Sorption coefficients for cerium, europium, and americium have been determined for a variety of rock samples from Yucca Mountain and in several groundwater compositions from the site (Thomas 1987; Knight and Thomas 1987). The data are generally consistent with the conclusions stated in the previous section. However, several additional points should be emphasized. First, experiments with rock samples that contained calcite (for example, G1-2901 and G2-723) or groundwater that was saturated with calcite (such as UE-25 p#1) showed very large sorption coefficients for these elements. This result suggests the radionuclides were either coprecipitated with carbonates (for example, calcite) or formed solid solutions on the surfaces of existing carbonates. Because groundwaters in the unsaturated zone at Yucca Mountain are likely near saturation with calcite, this observation suggests the trivalent lanthanides and actinides will not be mobile in the proposed repository horizon.

Second, experiments on samples with more than a few percent clay (for example, G1-3658) also showed high sorption coefficients. For these rock types, the ionic strength of the groundwaters may play a role in determining the magnitude of the sorption coefficients for these elements. Third, experiments with groundwaters containing high carbonate concentrations (such as UE-25 p#1) show large sorption coefficients for these elements, suggesting that carbonate complexation in solution

does not lead to significant decreases in the sorption coefficients for these elements in Yucca Mountain groundwaters.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The impact of variations in groundwater compositional parameters within the ranges expected in Yucca Mountain on the sorption behavior of actinium, americium, and samarium should be relatively minor. Over the expected pH range (6–9), the trivalent actinides and lanthanides appear to sorb primarily by inner-sphere surface-complexation mechanisms. These mechanisms are not sensitive to variations in ionic strength. Further, these elements appear to have high affinities for the mineral surfaces typically available in the Yucca Mountain rock units over the entire pH range expected. This result suggests that the trivalent actinide and lanthanide radionuclides will be strongly sorbed ($K_d > 100$ ml/g) over the entire range of expected groundwater compositions.

Plutonium

Behavior in solutions representative of Yucca Mountain groundwaters.

The solution behavior of the element plutonium is the most complicated of all the elements of interest and the least understood, particularly in near-neutral solutions representative of water compositions expected within the Yucca Mountain flow system. Plutonium can have several oxidation states in a given solution, and it can form complexes with a variety of ligands.

According to Nitsche et al. (1992, 1994), plutonium will be present in the +3, +4, +5, and +6 oxidation states in solutions representative of water compositions expected within Yucca Mountain. The +5 and +6 oxidation states should predominate in solution at redox potentials in the range of 230 to 350 mV. In J-13 and UE-25 p#1 waters, the +5 oxidation states should be dominant (60–80%) at 25°C. Most of the remaining plutonium in solution is in the +6 oxidation state in J-13 water and

the +4 oxidation state in UE-25 p#1 water.

Experimentally determined solubilities range from 3.0×10^{-7} to 1.0×10^{-6} M at 25°C. The solubility-controlling solids were found to be mixtures of polymeric Pu(IV) and smaller amounts of plutonium carbonates. The solubilities measured at pH values of 6 and 7 are consistent with the data reported by Rai et al. (1980). However, the solubilities measured for a pH of 8.5 exceed those reported by Rai et al. for amorphous $\text{Pu}(\text{OH})_4$ in 0.0015 M CaCl_2 . This result suggests that carbonate complexation of plutonium is significant at a pH of 8.5 in the Yucca Mountain groundwaters.

At 60°C, the +6 oxidation state was dominant (> 80%) in the UE-25 p#1 water at all three pH values. In J-13 water, the +5 and +6 oxidation states were present in nearly equal amounts (50%) at a pH of 7, whereas the +5 state dominated (60%) at a pH of 8.5 and the +6 state dominated (70%) at a pH of 6.

Experimentally determined solubilities at 60°C in J-13 water ranged from 2.7×10^{-8} M at a pH of 6 to 1.2×10^{-7} M at a pH of 8.5. For UE-25 p#1 water, the solubilities ranged from 4.5×10^{-7} M at a pH of 7 to 1.0×10^{-6} M at a pH of 8.5. The solubility-controlling solids at 60°C were found to be amorphous Pu(IV) polymer and PuO_2 .

The speciation of plutonium in these solutions could not be determined due to the low solubilities of plutonium in these water compositions relative to the detection limits of the available spectroscopic techniques. Modeling calculations with the EQ3 speciation computer code suggest that in J-13 water at 25°C the plutonyl ion and various carbonate complexes are most important at pH values from 6 to 7, whereas carbonate complexes and hydrolysis products are most important at a pH of 8.5 (Nitsche 1991). Speciation in the UE-25 p#1 water has not been modeled.

It is noteworthy that the experimentally determined redox behavior of plutonium in solution was quite

distinct from the behavior predicted on the basis of EQ3 calculations (Nitsche 1991). The causes for the differences in measured and calculated behavior have not been defined. They could involve various types of kinetic effects, including radiolysis effects, as well as the quality of the literature data in the EQ3 database. In any case, the uncertainties in our knowledge of the solution behavior of plutonium will make it difficult to properly interpret the sorption behavior of that element.

Qualitative evidence for behavior in the surficial environment.

Although naturally occurring plutonium has been detected at ultratrace levels in the environment, there is little documentation of the chemical controls on the mobility of this plutonium. However, anthropogenic plutonium has been present in the environment for decades. Data on the environmental behavior of this plutonium provide some indications of the behavior to be anticipated for plutonium emplaced in the proposed repository at Yucca Mountain.

Various papers in the literature discuss the transport of plutonium in the surficial environment around process stream outfalls or burial sites (for example, Means et al. 1978; Price and Ames 1978; Polzer et al. 1983). Unfortunately, the data on plutonium transport discussed in these papers are difficult to apply to the Yucca Mountain site because the waste streams included various types of organic ligands (for example, EDTA) that tend to enhance the transport of plutonium at these sites. In addition, the initial pH of many of these waste streams was in the acid range (2–4). Low pH conditions are not expected in the Yucca Mountain flow system. Organic ligands may be present at trace levels in this flow system, but they are not expected to play a major role in radionuclide transport.

The results of studies of plutonium transport in areas exposed to physical dispersal processes (for example, safety tests of nuclear weapons) are also difficult to interpret because of subsequent disturbances of the surface soils by wind, burrowing ani-

mals, construction activities, and so forth (for example, Essington et al. 1978).

Studies of the fate of global fallout for atmospheric nuclear weapons tests are more appropriate to the prediction of the transport of plutonium from a potential repository at Yucca Mountain. Most of these studies have involved the measurement of plutonium activities in seawater, lake water, and associated sediments (for example, Sholkovitz 1983). In general, these studies find that the bulk of the fallout-derived plutonium is present in the sediments with minor concentrations found in the waters. Interestingly, the plutonium present in the waters is often an oxidized form (that is, +5 or +6), whereas the fraction in the sediment is thought to be a reduced form (Waters 1983). "Distribution coefficients" have been calculated based on the water and sediment plutonium concentrations even though the water and sediment samples may be from areas that are separated by tens of kilometers. This makes it difficult to evaluate the calculated distribution coefficients in relation to sites such as the potential repository in Yucca Mountain.

More pertinent perhaps are the measurement of plutonium concentrations in oceanic sediments and their associated pore waters (Buesseler and Sholkovitz 1987). Such studies invariably yield sorption coefficients for plutonium in the range of 10^3 to 10^5 mg/l with the lower values observed in the more oxidized sediments. Given the high ionic strength of seawater (that is, the pore waters), these data suggest that ionic-strength effects are not an issue in the plutonium sorption behavior in natural systems. However, complexation of plutonium by carbonate can be significant and appears to be the cause for elevated plutonium activities in several high alkalinity (0.3–3.0 M) lakes in the western United States (Sanchez et al. 1985). Because alkalinity values are expected to be orders of magnitude lower within the Yucca Mountain flow system relative to the levels found in these lakes, carbonate complexation in the solution phase should not be an issue at this site.

An important aspect of all the studies on plutonium sorption behavior is the issue of redox disequilibrium. In seawater and many lake waters, the inorganic species of plutonium in solution appears to be dominated by the +5 and +6 oxidation states with the +3 and +4 states present at much lower concentrations (Waters 1983). In the solid phase, the oxidation state is thought to be predominantly +4. This aspect of plutonium solution chemistry has been studied in the laboratory for many years and appears to involve various disproportionation reactions that are not fully understood (for example, Newton et al. 1986).

The question of concern to the present study is how groundwater compositional parameters will effect this redox disequilibrium and, in turn, the sorption behavior of plutonium. In the disproportionation experiments reported by Newton et al. (1986) and in the solubility experiments reported by Nitsche et al. (1992, 1994), plutonium concentrations in the experiments were sufficiently high that radiation effects were evident. An important question is "If plutonium is present at trace levels and not in contact with a 'pure' plutonium compound, are disproportionation reactions still a factor?" If they are not, then the next question would be "What is the stable oxidation state of plutonium when it is present at trace levels in Yucca Mountain groundwaters?" If the +5 or +6 oxidation states of plutonium are the dominant stable states in groundwaters such as those found within Yucca Mountain, as suggested by the experiments of Nitsche et al. (1992, 1994), then plutonium might be as mobile as neptunyl in the far-field of the potential repository, assuming it is present as the plutonyl ion or its complexes. On the other hand, if the +4 or +3 oxidation states are the dominant stable states in these groundwaters, this element would likely behave as other +3 and +4 actinides and be strongly sorbed with minimal migration potential.

Data from laboratory sorption experiments.

Allard (1982) reported results on experiments involving plutonium sorption on quartz, apatite, attapulgite, montmorillonite, and various minerals

rich in ferrous iron in a dilute groundwater containing plutonium at 1.8×10^{-11} M. For all the minerals, the sorption coefficients were greater than 10^3 ml/g over a pH range from 4 to 9. Apatite, attapulgite, biotite, and montmorillonite showed sorption coefficients greater than 10^4 ml/g over this pH range. Torstenfelt et al. (1988) presented data for plutonium sorption on feldspars, clays, and granite in contact with J-13 water. The sorption coefficients reported by them are generally between 100 to 200 ml/g in neutral to alkaline solutions. These authors emphasized the importance of proper experimental technique in the determination of sorption coefficient values for plutonium and noted the potential for colloid formation in these types of experiments. Data indicating high affinity of plutonium for ferric oxyhydroxide, manganese oxide, and carbonate mineral surfaces were presented by Means et al. (1978), Keeney-Kennicutt and Morse (1985), and Sanchez et al. (1985). Means et al. noted that manganese oxides sorb plutonium more strongly than ferric oxyhydroxides in natural environments (presumably as a result of redox reactions on the manganese-oxide surface).

Measurements of plutonium sorption coefficients involving Yucca Mountain rock samples and J-13 groundwater were summarized by Thomas (1987). Additional measurements involving other groundwater compositions were reported by Lawrence (1988). The following observations are considered the most significant. First, the values measured for the plutonium sorption coefficient range from 20 to greater than 4,500 ml/g with most values lying between 100 to 2,000 ml/g at a pH of from 8.2 to 8.8. Second, the coefficients determined during the desorption experiments were occasionally in the range of the sorption coefficient values, but more typically, they were 10 to 20 times larger, reflecting the irreversibility of the sorption reactions. Third, zeolitic samples typically had lower sorption coefficient values than vitric or devitrified samples. It appears that rocks that have essentially no reduction capacity remaining (that is, samples lacking ferrous iron or sulfide) show the lowest sorption coefficients for plutonium. Fourth, sam-

ples with calcite or clay showed the largest sorption coefficients ($> 4,500$ ml/g for samples with 30% calcite). Fifth, based on the six to eight experiments for which data are available, there was up to a factor of twelve variation in sorption coefficients as a function of groundwater composition. Water from well UE-25 p#1 was associated with the largest values (240–540 mg/l, sorption-desorption) with waters from wells H-3 and J-13 showing the lowest values (20–230 ml/g). The higher values obtained with UE-25 p#1 water may reflect calcite precipitation. Sixth, there did not appear to be a dependence of the sorption coefficient on pH over the range from 7 to 9, although the available data are limited on this issue. Seventh, there was less than a factor of four dependence of the sorption coefficient on radionuclide concentration over the range from 10^{-9} to 10^{-12} M.

Conclusions that can be drawn from these data include: 1) the plutonium sorption coefficient will be greater than 100 ml/g for most of the groundwater and rock compositions likely to be encountered within Yucca Mountain; 2) calcite and clay promote plutonium sorption/coprecipitation and may retard plutonium migration in fractures; and 3) the redox state of the groundwaters and of the rock units in which they occur may be critical to the sorption behavior of plutonium.

We studied the sorption of plutonium onto the three main types of tuff in J-13 water (under oxidizing conditions) using a carbon-dioxide overpressure (to obtain a pH of 7). To identify the sorbing minerals in the tuffs, we also studied sorption onto the pure minerals hematite, clinoptilolite, albite, and quartz. The results of the batch-sorption experiments for plutonium are summarized in Fig. 21. Because plutonium sorbs onto nongeologic media, the batch-sorption distribution coefficients reported in Fig. 21 are based on the concentration of plutonium in the control solutions. The affinity of tuffs for plutonium at a pH of 7 in decreasing order is zeolitic $>$ vitric $>$ devitrified. The affinity of minerals for plutonium in decreasing order is hematite $>$ clinoptilolite $>$ albite $>$

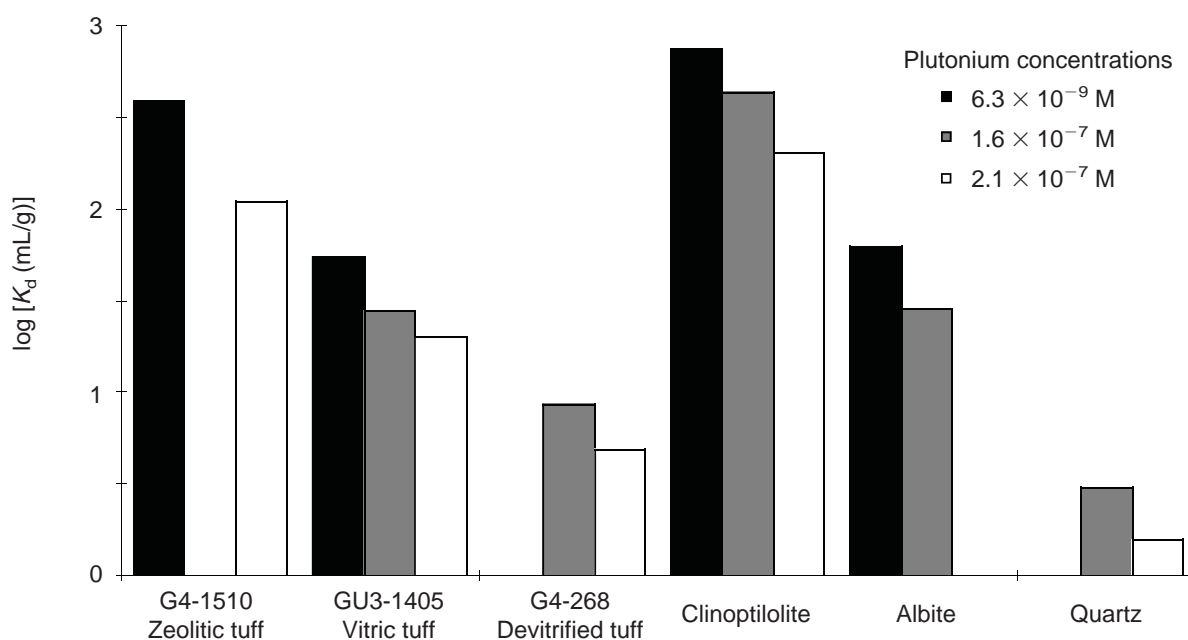


Figure 21. Plutonium Sorption. The logarithm of the batch-sorption distribution coefficient, $\log K_d$, is shown for the sorption of plutonium in J-13 well water at a pH of 7 and the specified initial plutonium concentrations. All solids, except clinoptilolite, were wet sieved to particle sizes ranging from 75 to 500 μm . The periods of pretreatment and sorption were each 3 days.

quartz. Inspection of Fig. 21 indicates that plutonium sorption is nonlinear in the concentration range from 6×10^{-9} to 2×10^{-7} M.

Nitsche et al. (1993a) report that even when a plutonium solution in J-13 or UE-25 p#1 water is prepared starting in the +4 oxidation state, the predominant final oxidation state is +5, or Pu(V). The solution used for our plutonium sorption experiments was prepared from a well-characterized Pu(V) acidic stock in J-13 well water. Consequently, it would be reasonable to assume that the plutonium would have remained predominantly in the +5 oxidation state in the solution used for the sorption studies.

Comparison of the data of Fig. 21 with the results of similar experiments with neptunium and uranium indicates that significant plutonium sorption occurred in tuffs and minerals that exhibit very small sorption of Np(V) and U(VI). This result is very puzzling; if plutonium in J-13 well water is

predominantly Pu(V) and Pu(VI), it is expected that its sorption behavior would have been similar to that observed for Np(V) and U(VI). Several possible explanations of the plutonium sorption results are: 1) Nitsche's data for the oxidation states are incorrect, and the predominant plutonium oxidation state in J-13 well water at a pH of 7 is Pu(IV), not Pu(V) and Pu(VI); 2) the Pu(IV) species is what sorbs from J-13 water but a re-equilibration in the solution phase produces more Pu(IV) to maintain equilibrium (which implies that the kinetics of plutonium speciation in solution are fast); and 3) Pu(V) and Pu(VI) reduce to Pu(IV) at solid surfaces (as a result of changes in the solution redox potential in the presence of the solid phases).

The sorption of plutonium onto tuffs and minerals in J-13 and synthetic UE-25 p#1 water under atmospheric conditions was studied (Figs. 22 to 27) as a function of time and initial plutonium solution concentration. Inspection of these figures indicates that plutonium sorption is extremely slow

continued on page 73

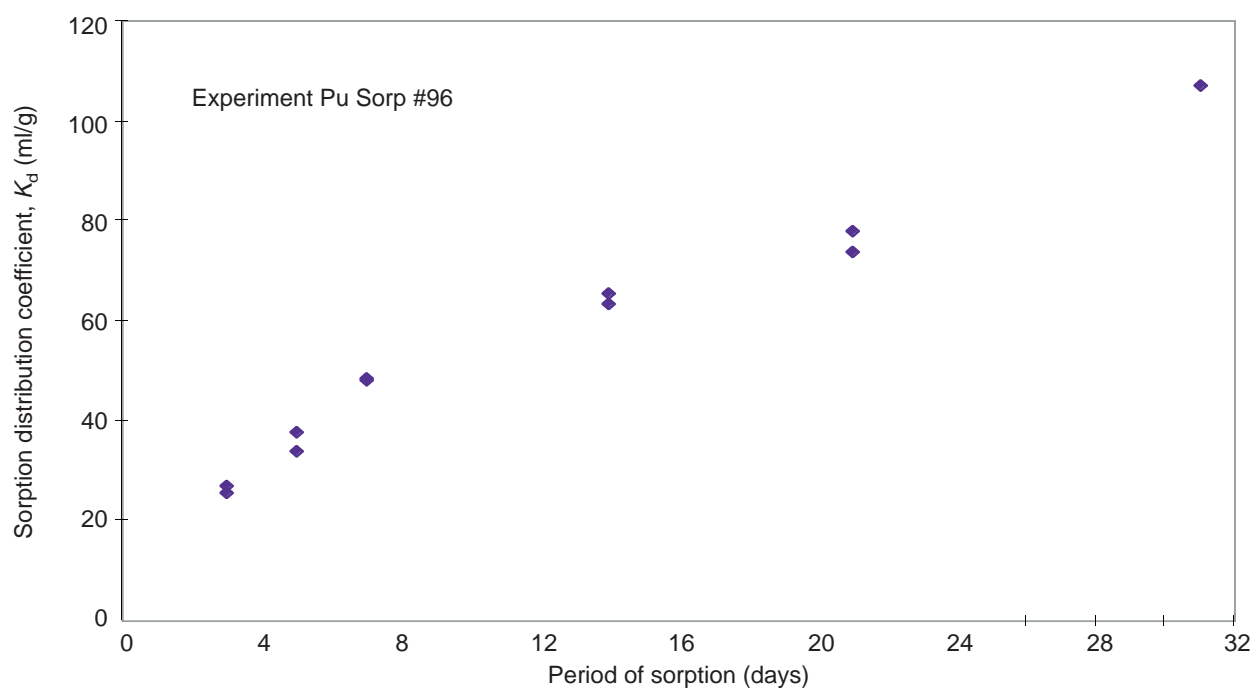


Figure 22. Plutonium Sorption onto Devitrified Tuff in J-13 Water. The plot shows plutonium sorption onto tuff sample G4-272 as a function of time under atmospheric conditions with an original plutonium concentration in J-13 well water of 2.4×10^{-7} M.

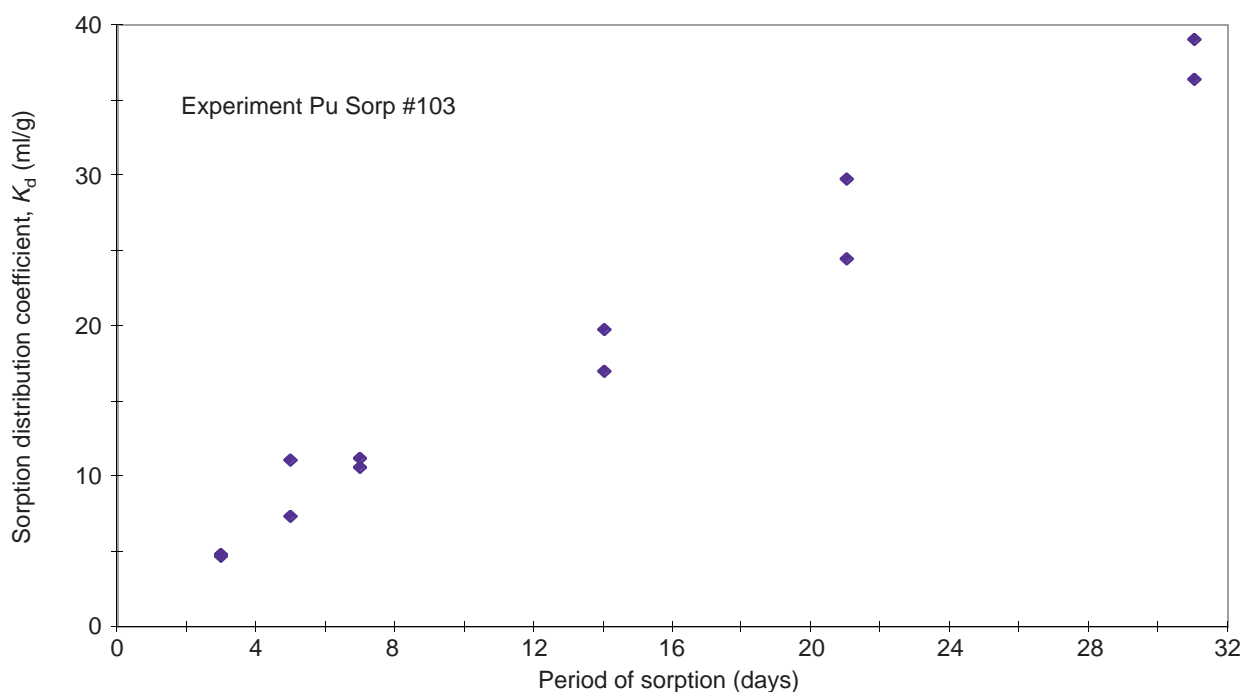


Figure 23. Plutonium Sorption onto Devitrified Tuff in Synthetic UE-25 p#1 Water. The plot shows plutonium sorption onto tuff sample G4-272 as a function of time under atmospheric conditions with an original plutonium concentration in synthetic UE-25 p#1 water of 2.4×10^{-7} M.

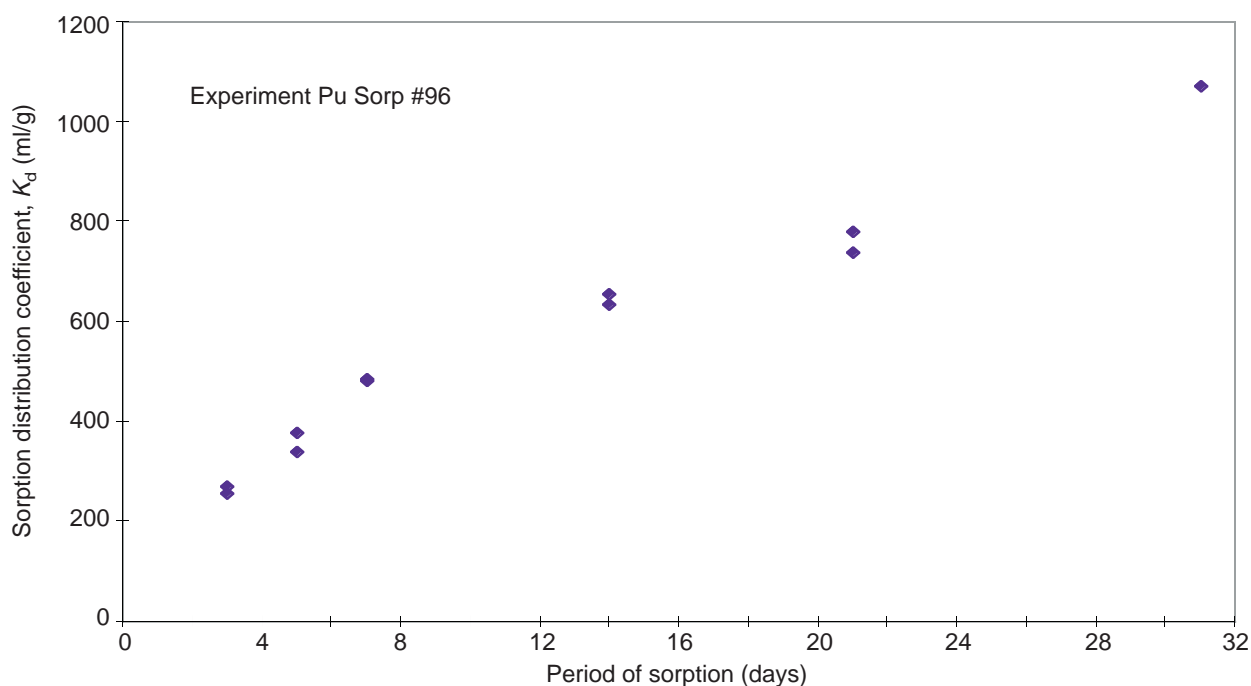


Figure 24. Plutonium Sorption onto Vitric Tuff in J-13 Water. This plot shows plutonium sorption onto tuff sample GU3-1414 as a function of time under atmospheric conditions with an original plutonium concentration in J-13 well water of 2.4×10^{-7} M.

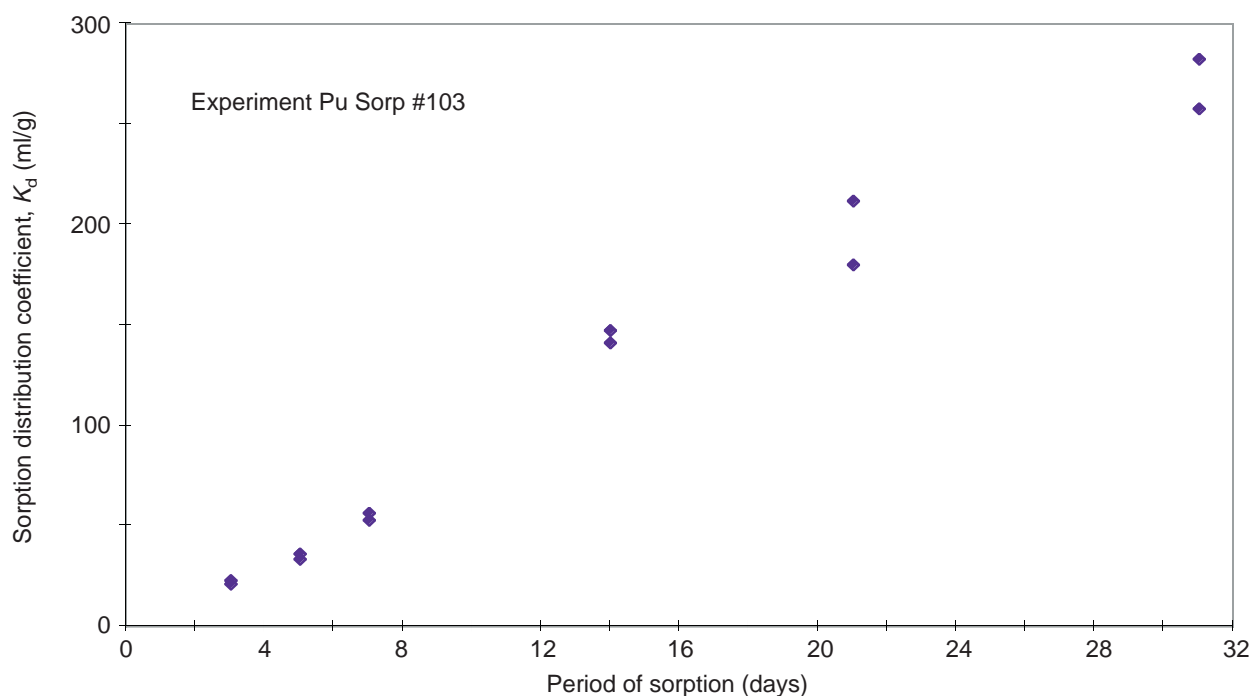


Figure 25. Plutonium Sorption onto Vitric Tuff in Synthetic UE-25 p#1 Water. The plot shows plutonium sorption onto tuff sample GU3-1414 as a function of time under atmospheric conditions with an original plutonium concentration in synthetic UE-25 p#1 water of 2.4×10^{-7} M.

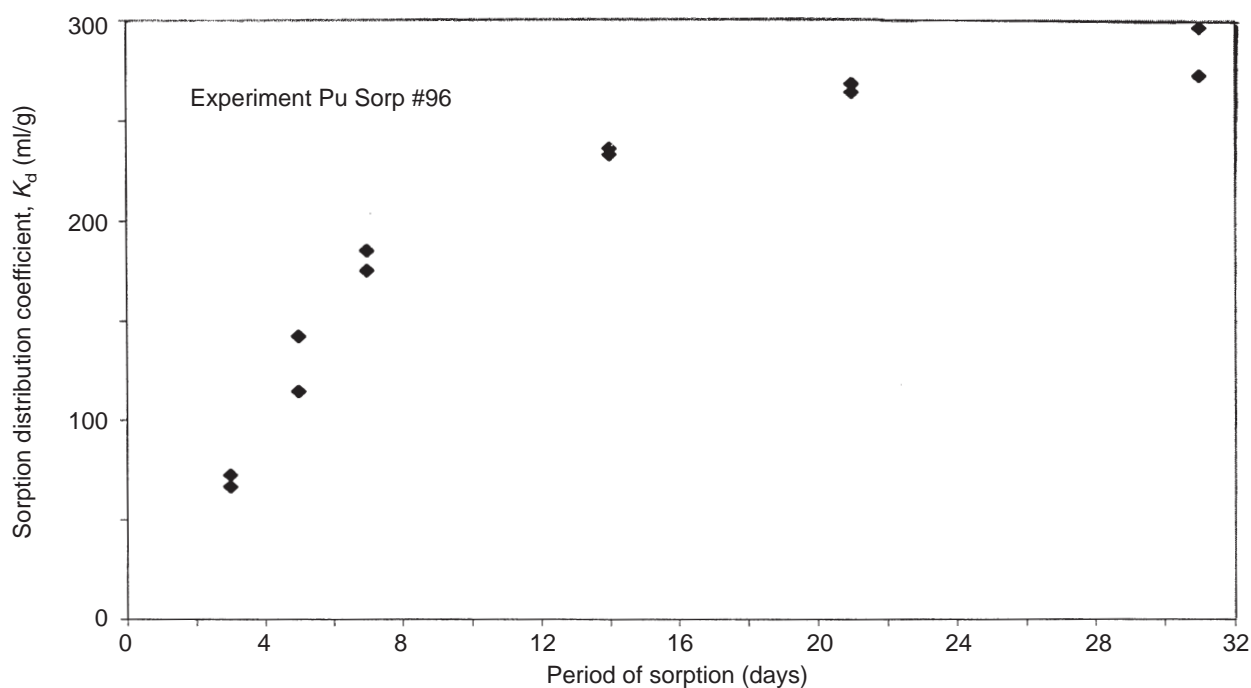


Figure 26. Plutonium Sorption onto Zeolitic Tuff in J-13 Water. This plot shows plutonium sorption onto tuff sample G4-1515 as a function of time under atmospheric conditions with an original plutonium concentration in J-13 well water of 2.4×10^{-7} M.

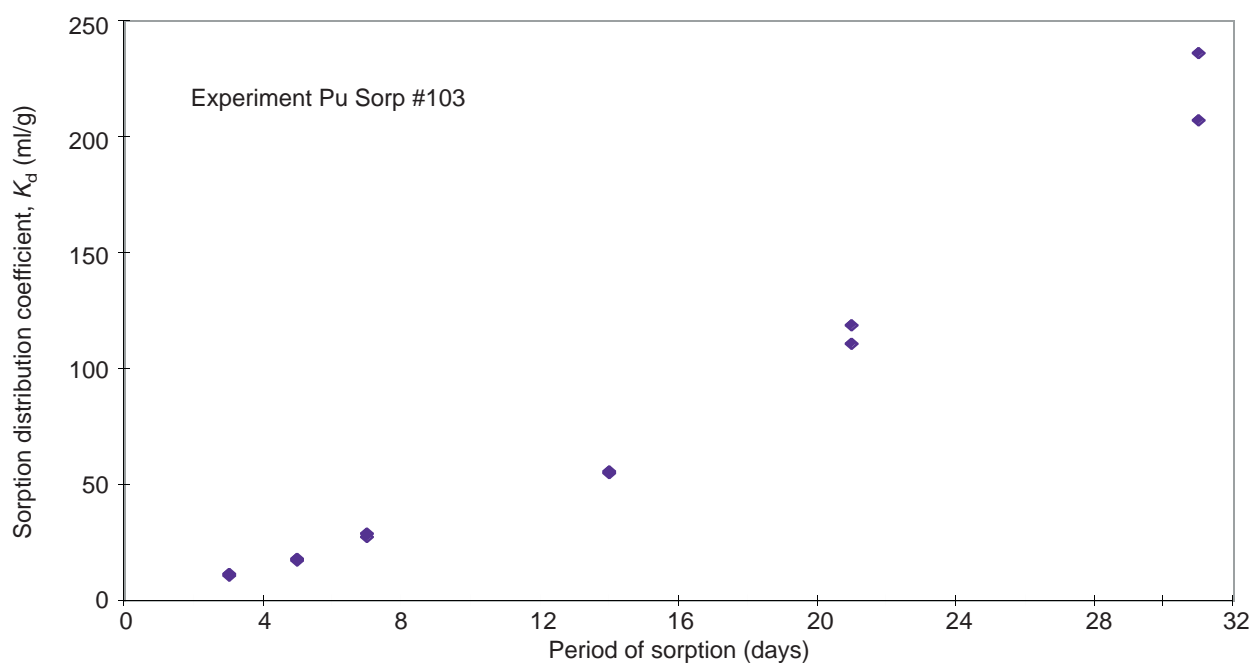


Figure 27. Plutonium Sorption onto Zeolitic Tuff in Synthetic UE-25 p#1 Water. The plot shows plutonium sorption onto tuff sample G4-1515 as a function of time under atmospheric conditions with an original plutonium concentration in synthetic UE-25 p#1 water of 2.4×10^{-7} M.

continued from page 69

(possibly due to a redox reaction at the solid surface). Even after 32 days of sorption, equilibration had not been achieved. The sorption of plutonium onto the tuffs and minerals is very substantial.

Table 13 summarizes the ranges for sorption distribution coefficients in Yucca Mountain groundwaters for plutonium. The sorption isotherms for plutonium (Figs. 28 to 45) indicate that plutonium sorption as a function of radionuclide concentration cannot be expressed using a K_d ; the isotherms are generally nonlinear. However, given the high affinity of Yucca Mountain tuffs for plutonium and the other observations made in this study, it appears that using a K_d to predict plutonium radionuclide transport in performance-assessment calculations will provide conservative predictions for the release of radionuclides.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters. On the basis of the discussion in the previous sections, it appears the most important groundwater compositional parameter in relation to plutonium sorption is the redox potential. Closely related to

this parameter is the abundance of ferrous iron in the rock units. Note that redox potentials in groundwaters may not reflect equilibrium with the host rock (Lindberg and Runnells 1984). Complexation reactions with inorganic ligands in solution and variations in solution pH appear to have less significant impacts on the sorption behavior of plutonium in Yucca Mountain rock-water systems.

Cesium, Radium, and Strontium

Behavior in solutions representative of Yucca Mountain groundwaters.

These elements show relatively simple solution behavior in typical groundwaters. They are not subject to changes in oxidation state in the groundwater compositions expected in Yucca Mountain. Radium and cesium are invariably present as the simple Ra^{2+} and Cs^+ cations in the expected groundwater compositions (Ogard and Kerrisk 1984). Strontium exists primarily as the Sr^{2+} ion in these waters but may also be present as the neutral aqueous species $SrSO_4$ at concentrations of a few per cent of the total strontium solution concentration (Ogard and Kerrisk 1984).

continued on page 83

Table 13. Plutonium Sorption Distribution Coefficients (under atmospheric conditions)

Solid Phase	K_d Range in J-13 Water (ml/g)	K_d Range in Synthetic UE-25 p#1 Water (ml/g)
Vitric tuff	600 – 2,000	100 – 400
Zeolitic tuff	300 – 500	100 – 400
Devitrified tuff	40 – 100	20 – 70
Synthetic hematite	> 10,000	> 10,000
Montmorillonite	> 10,000	> 10,000
Clinoptilolite	600 – 3,000	2,000 – 5,000
Calcite	200 – 1,000	100 – 800
Gibbsite	0 – 10	10 – 90
Albite	3 – 10	< 10
Quartz	< 10	< 10

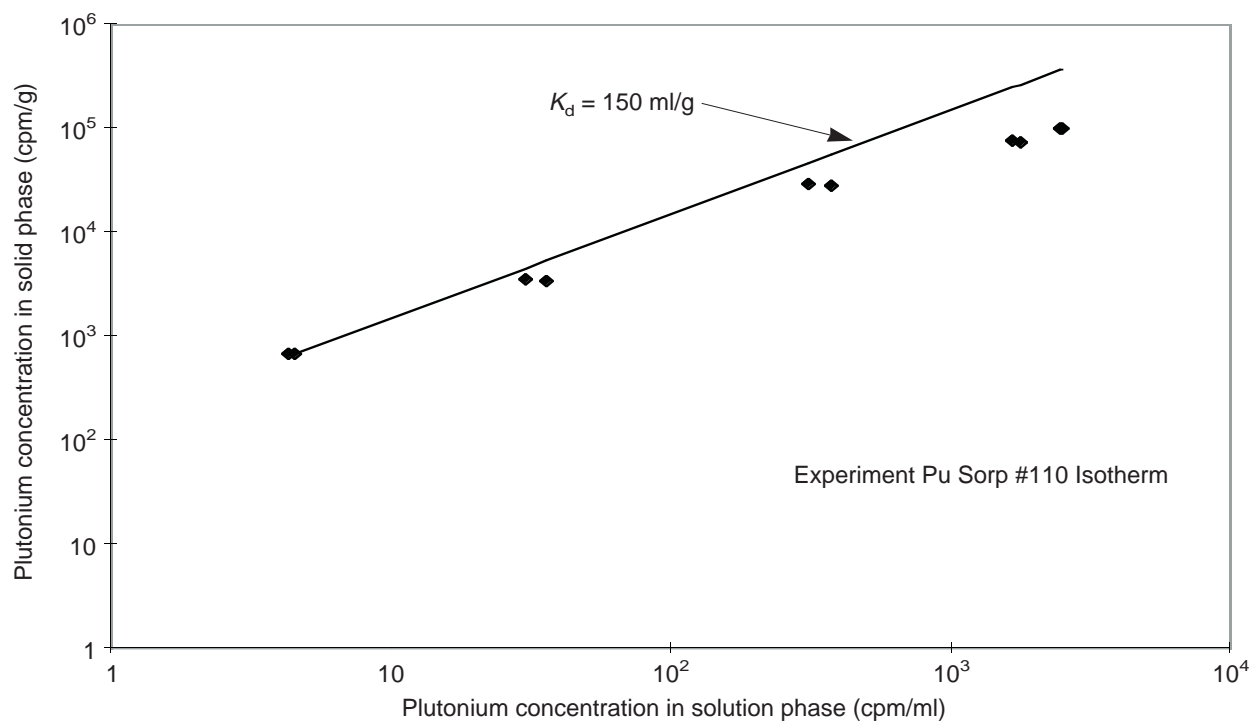


Figure 28. Plutonium Isotherm for Devitrified Tuff in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto the tuff sample G4-272 under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

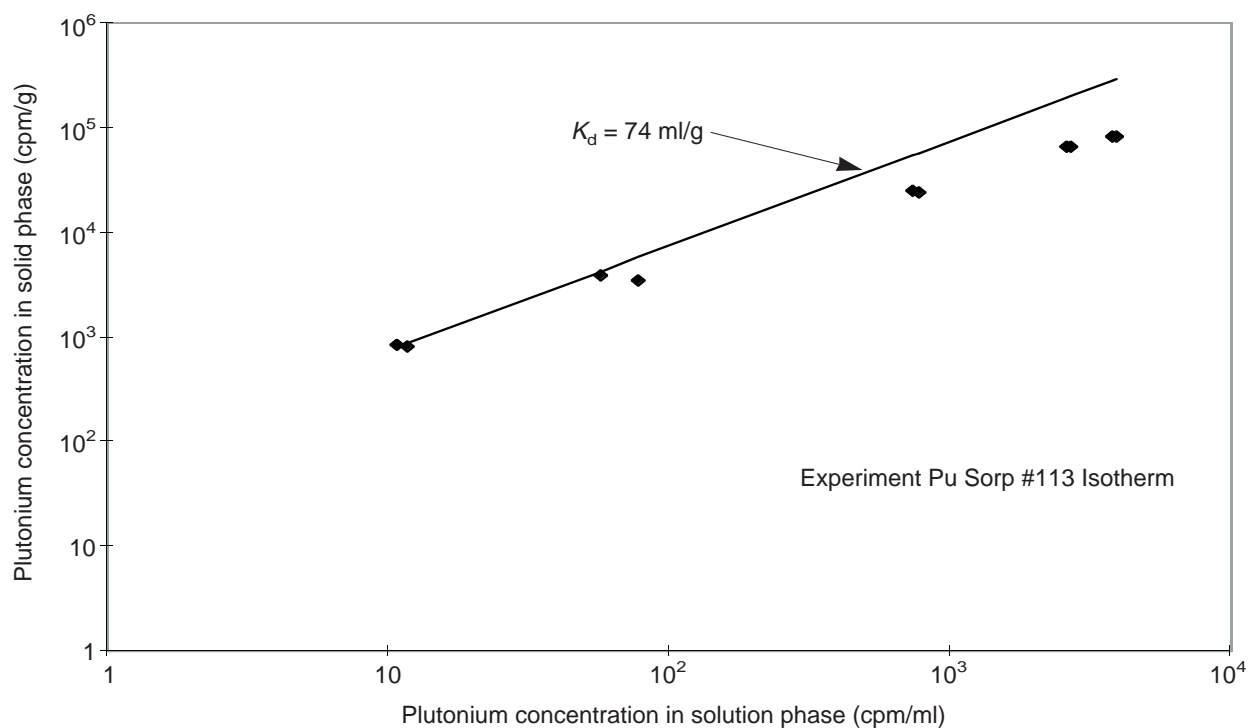


Figure 29. Plutonium Isotherm for Devitrified Tuff in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto the tuff sample G4-272 under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

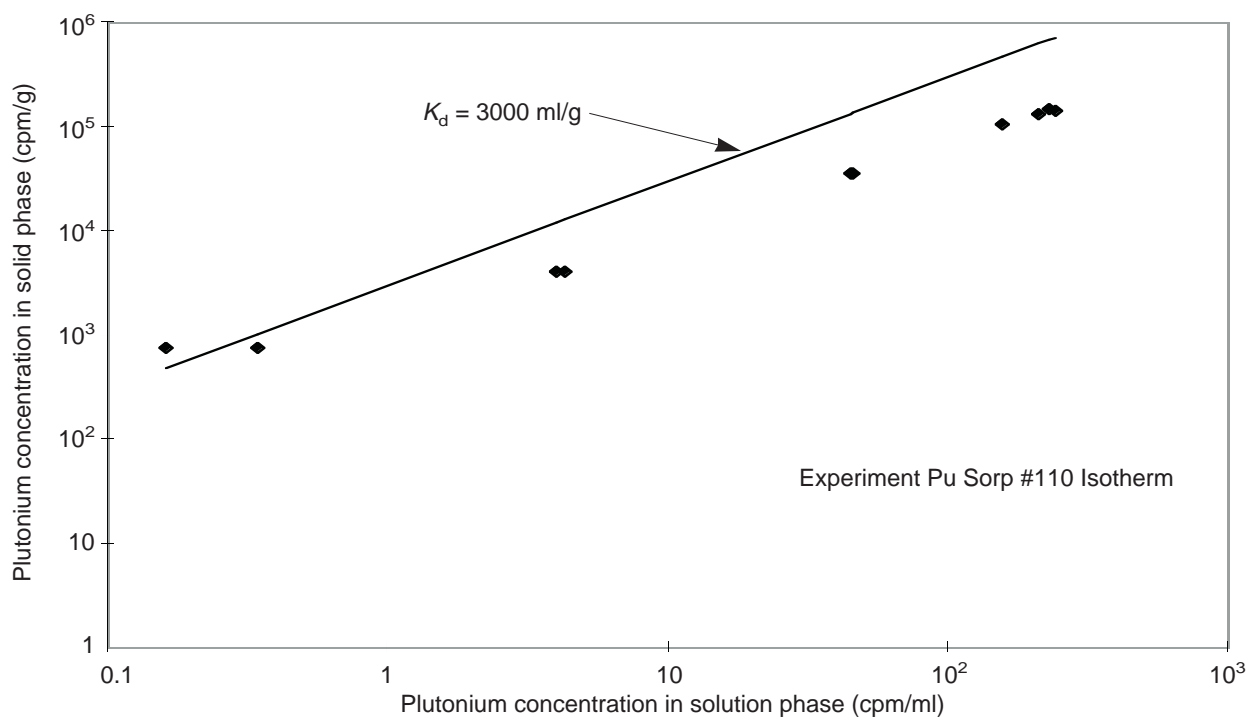


Figure 30. Plutonium Isotherm for Vitric Tuff in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto the tuff sample GU3-1414 under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

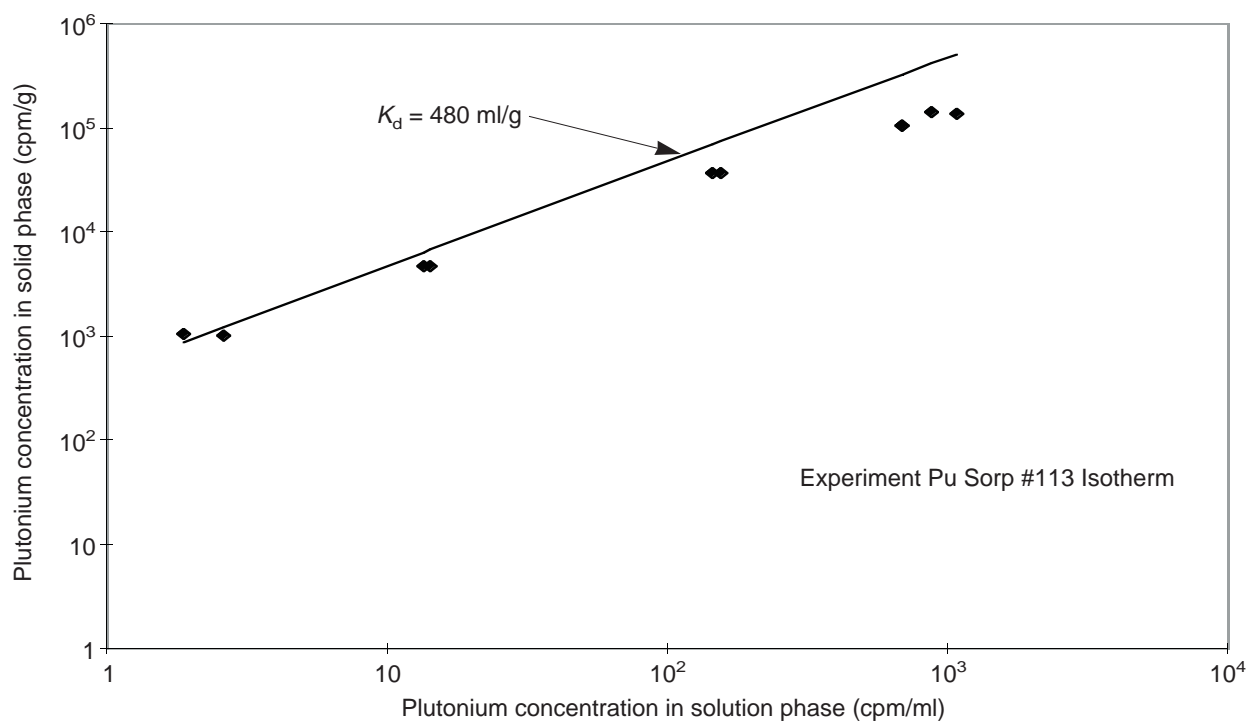


Figure 31. Plutonium Isotherm for Vitric Tuff in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto the tuff sample GU3-1414 under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

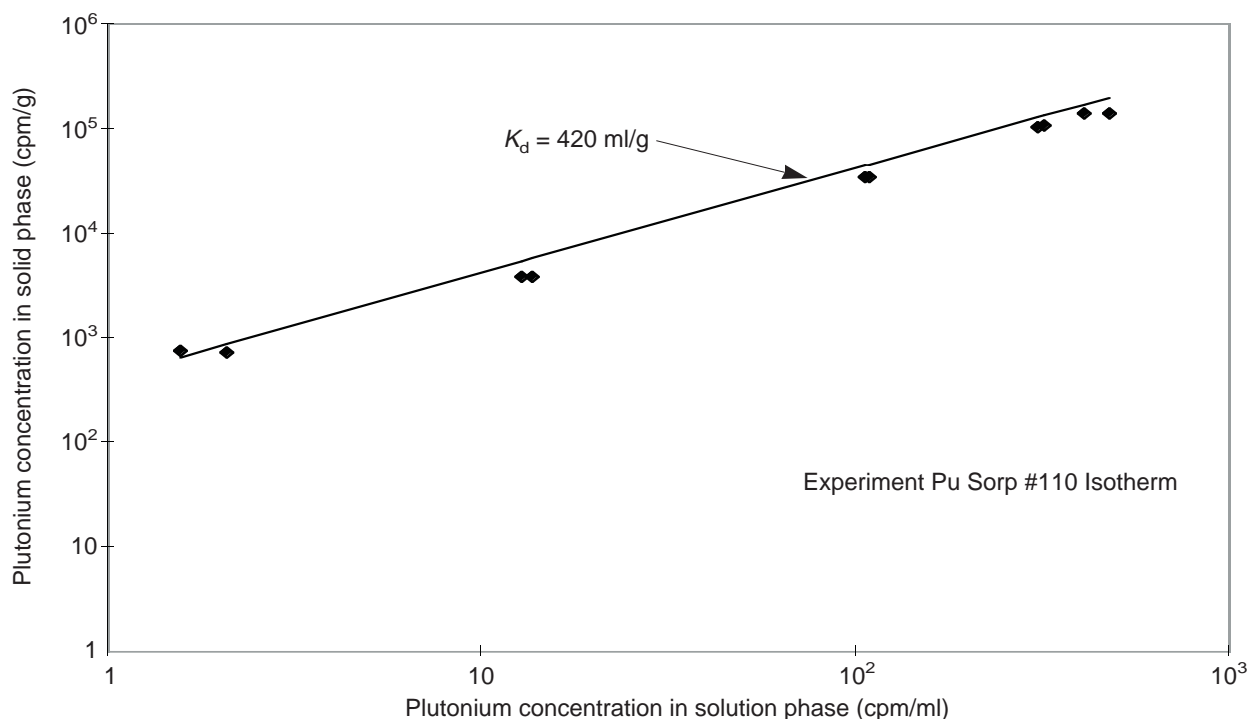


Figure 32. Plutonium Isotherm for Zeolitic Tuff in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto the tuff sample G4-1515 under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

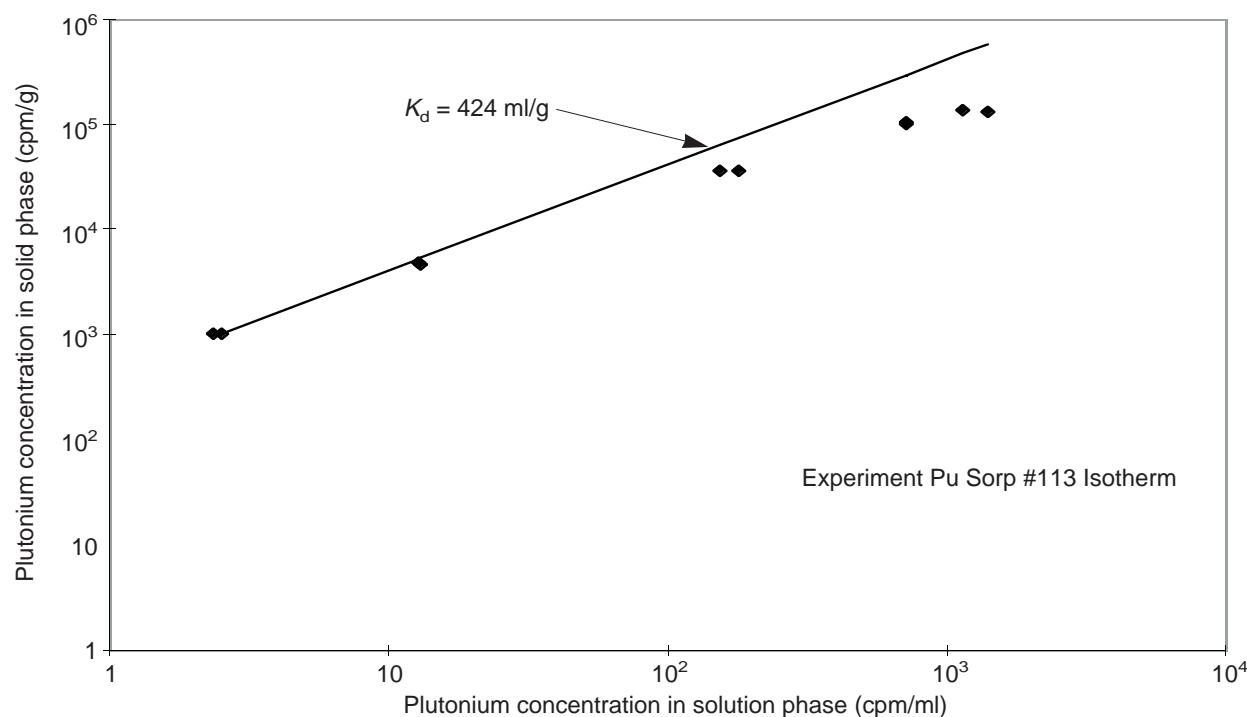


Figure 33. Plutonium Isotherm for Zeolitic Tuff in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto the tuff sample G4-1515 under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

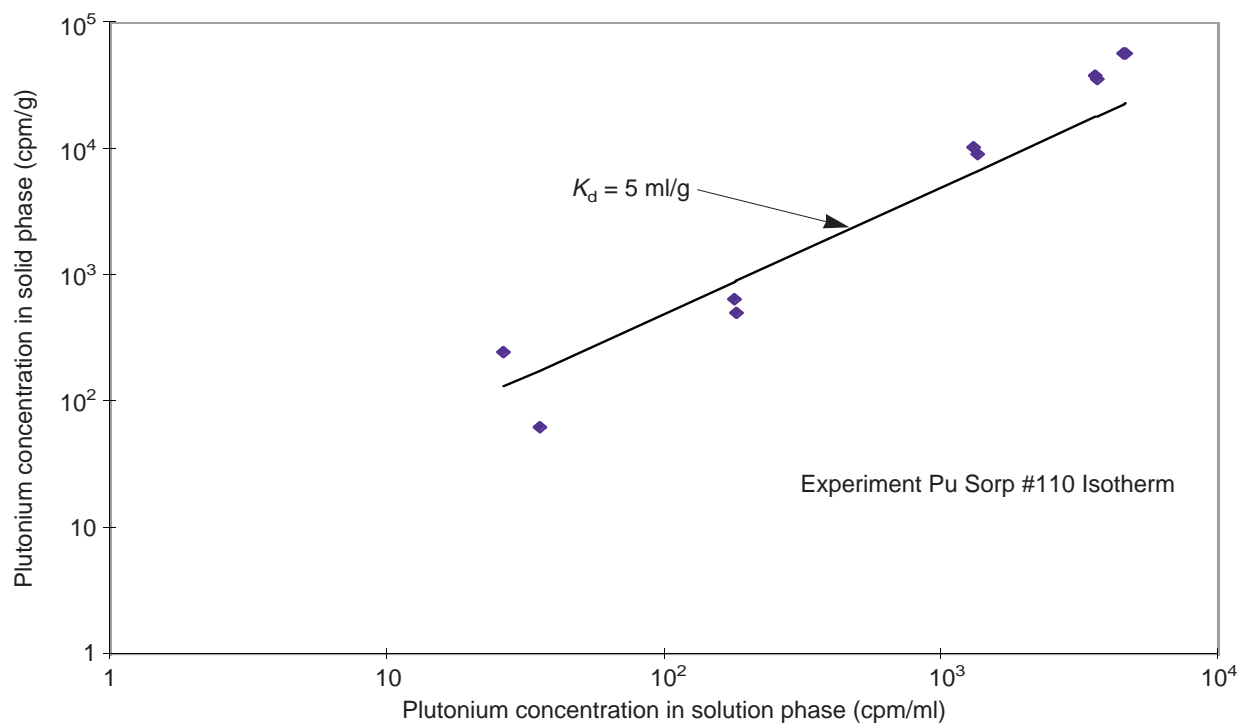


Figure 34. Plutonium Isotherm for Albite in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto albite under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

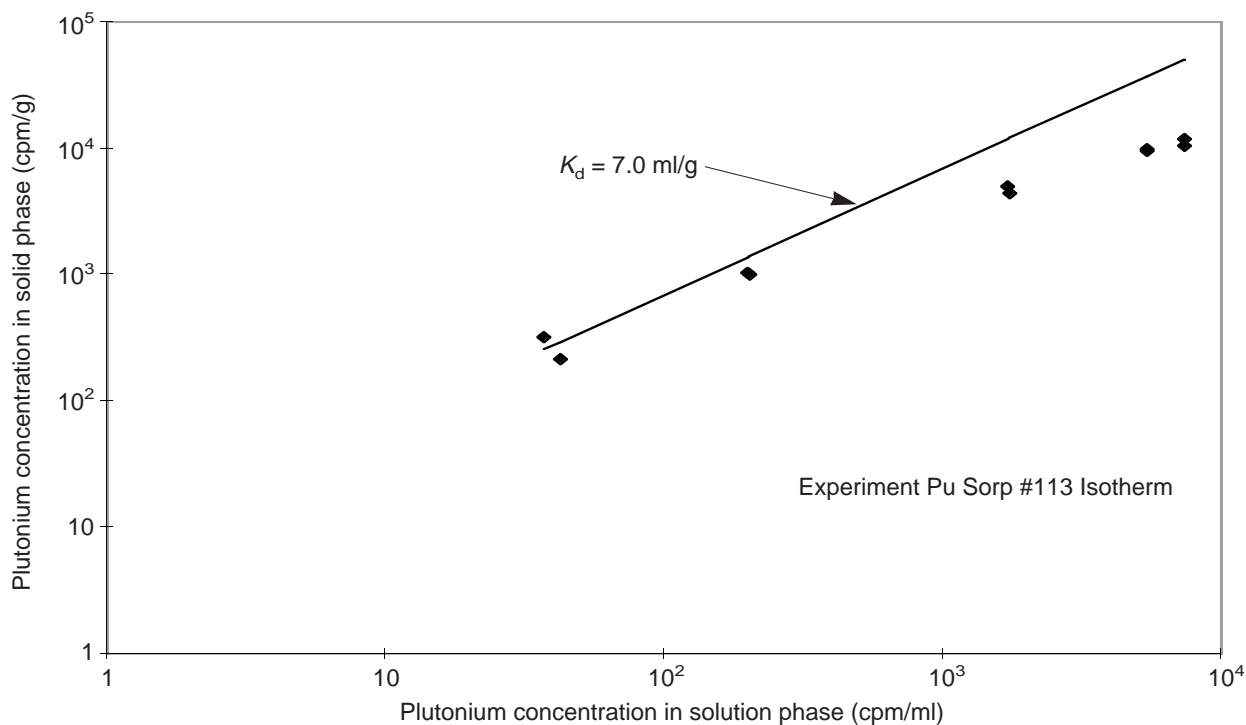


Figure 35. Plutonium Isotherm for Albite in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto albite under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

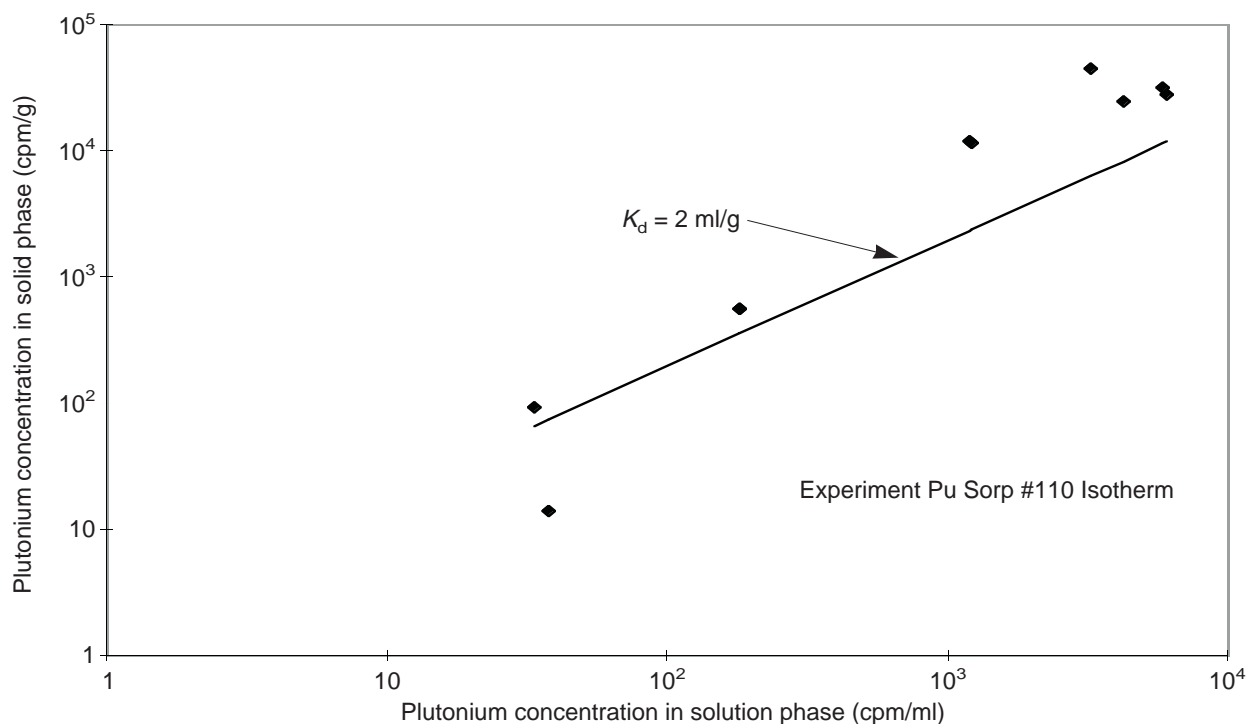


Figure 36. Plutonium Isotherm for Gibbsite in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto gibbsite under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

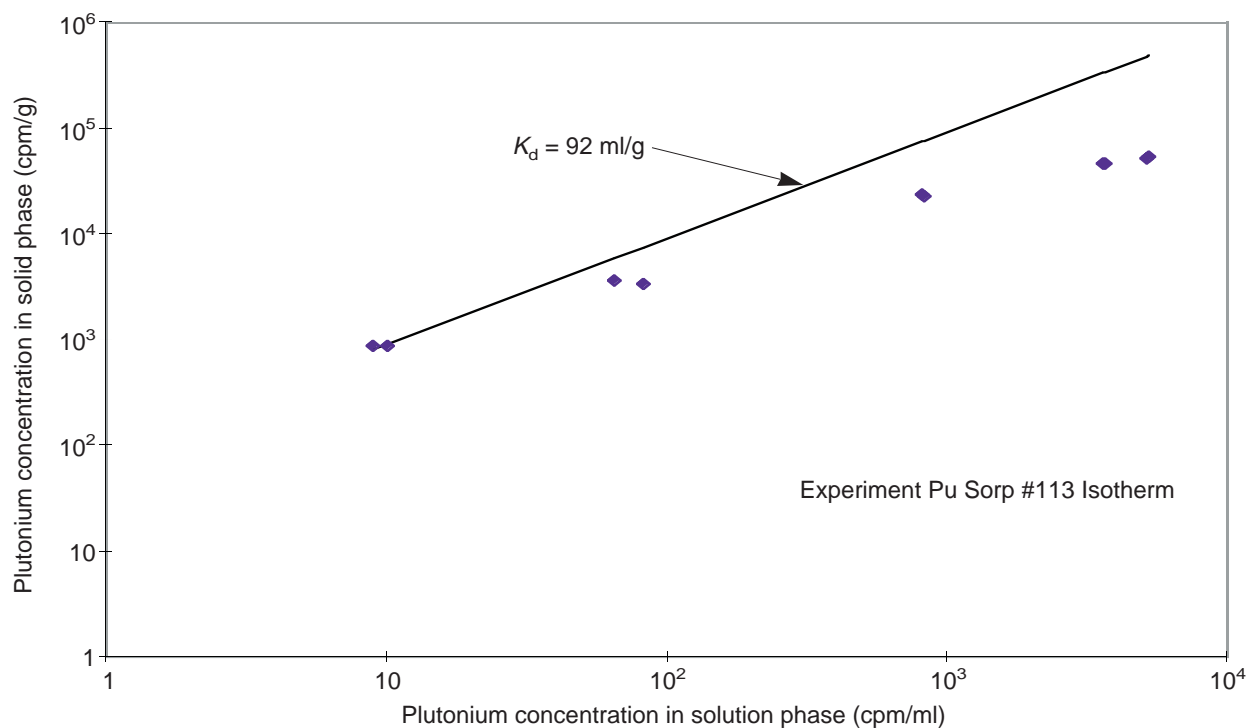


Figure 37. Plutonium Isotherm for Gibbsite in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto gibbsite under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

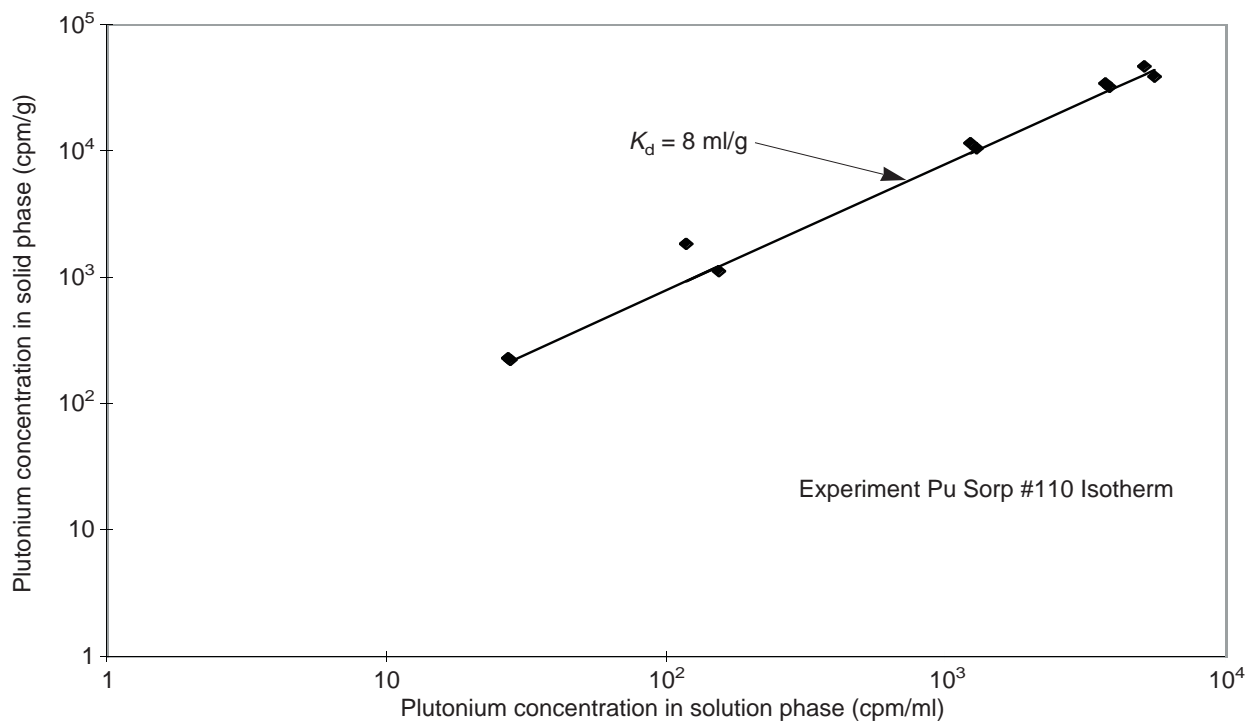


Figure 38. Plutonium Isotherm for Quartz in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto quartz under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

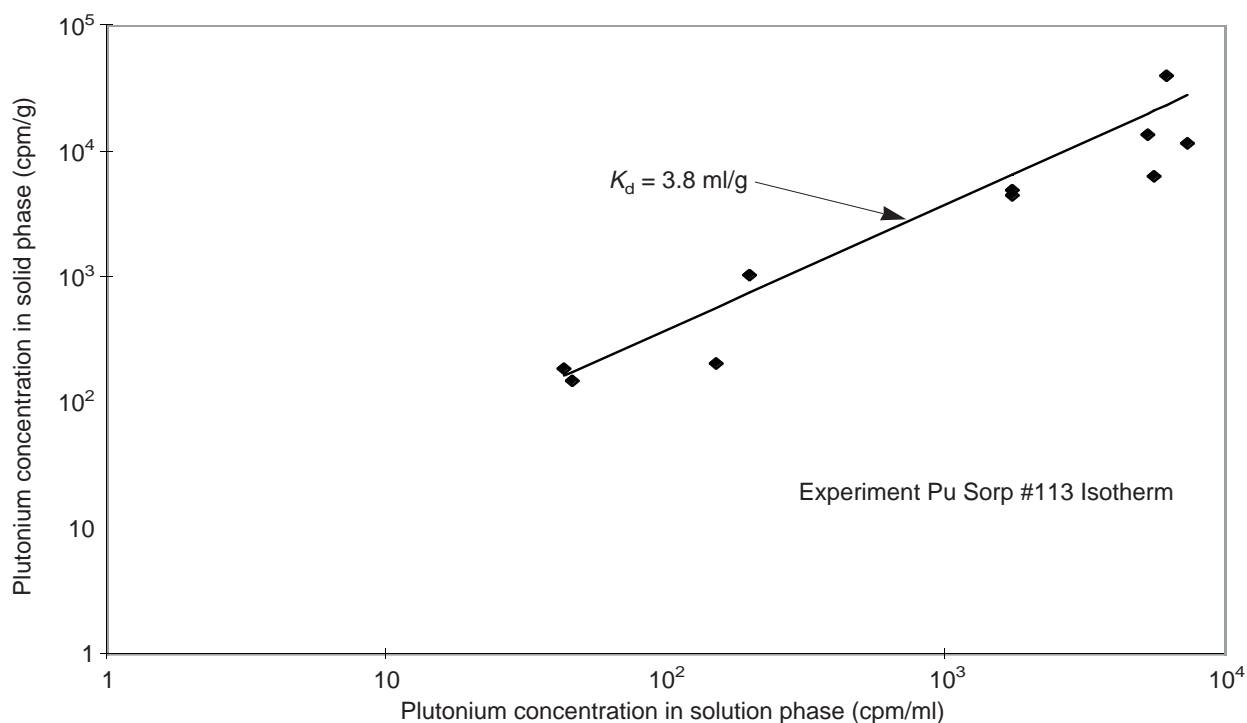


Figure 39. Plutonium Isotherm for Quartz in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto quartz under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

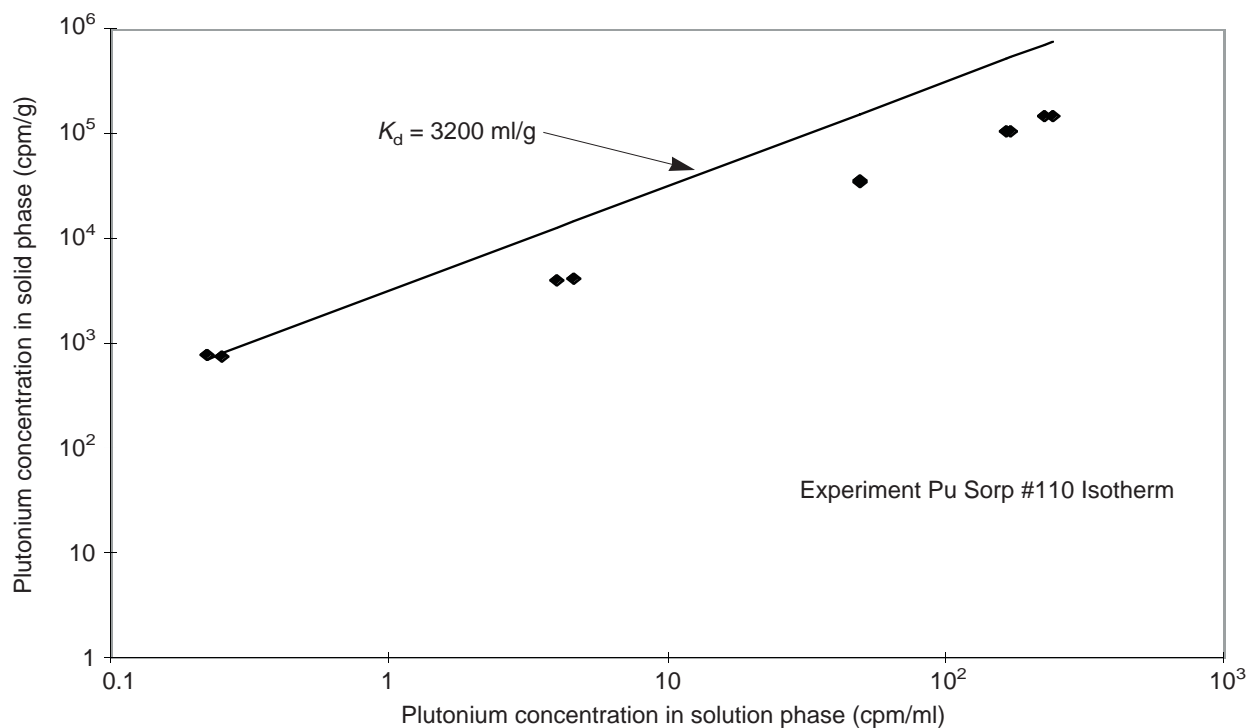


Figure 40. Plutonium Isotherm for Clinoptilolite in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto clinoptilolite under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

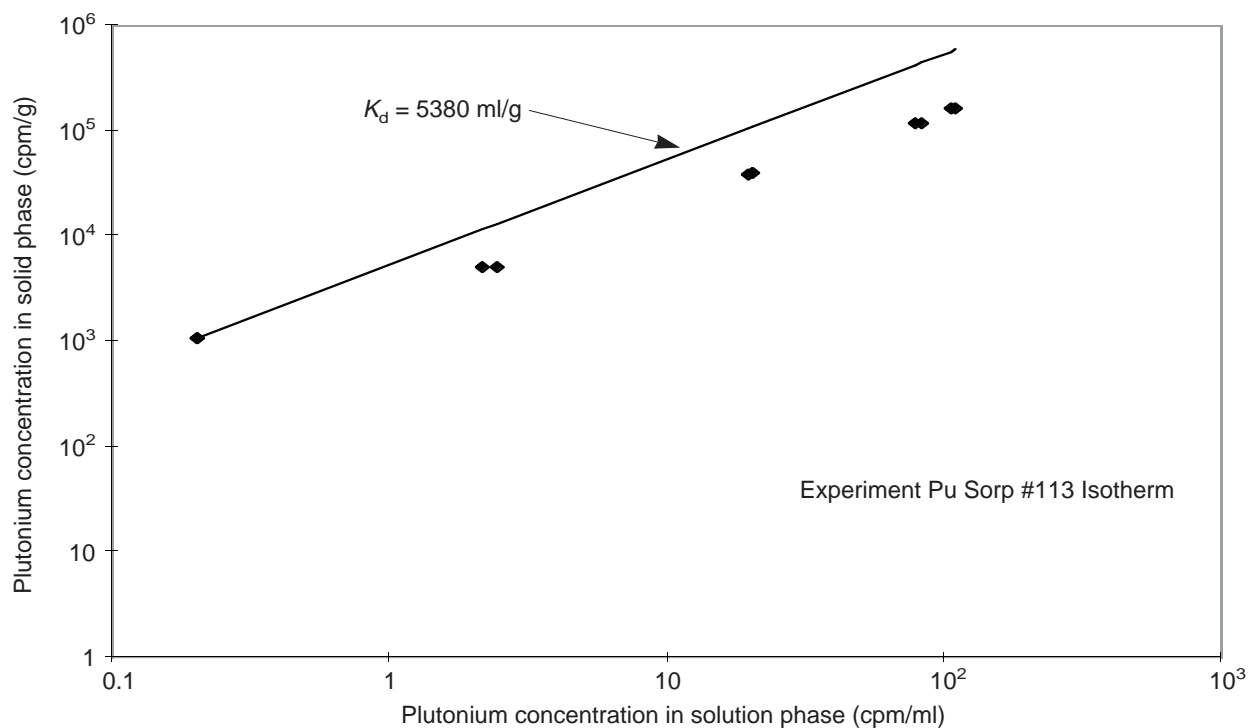


Figure 41. Plutonium Isotherm for Clinoptilolite in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto clinoptilolite under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

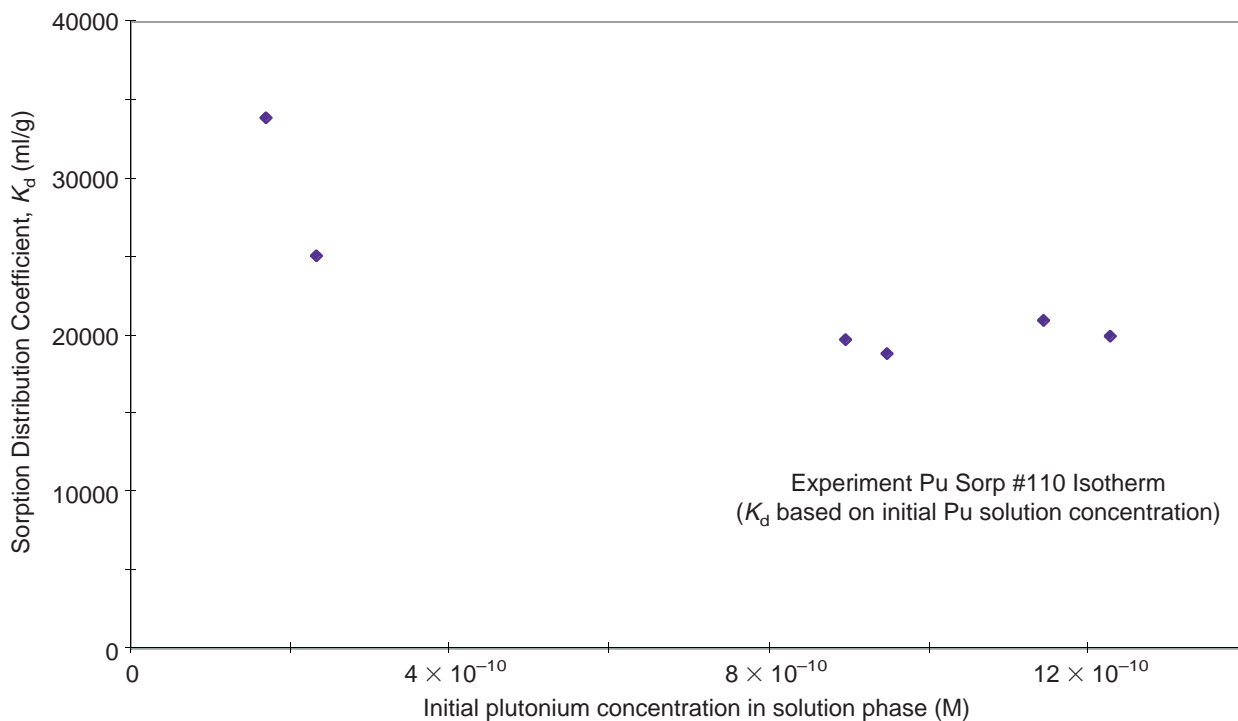


Figure 42. Plutonium Isotherm for Montmorillonite in J-13 Water. This plot shows plutonium sorption distribution coefficients (diamonds) for sorption onto montmorillonite under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

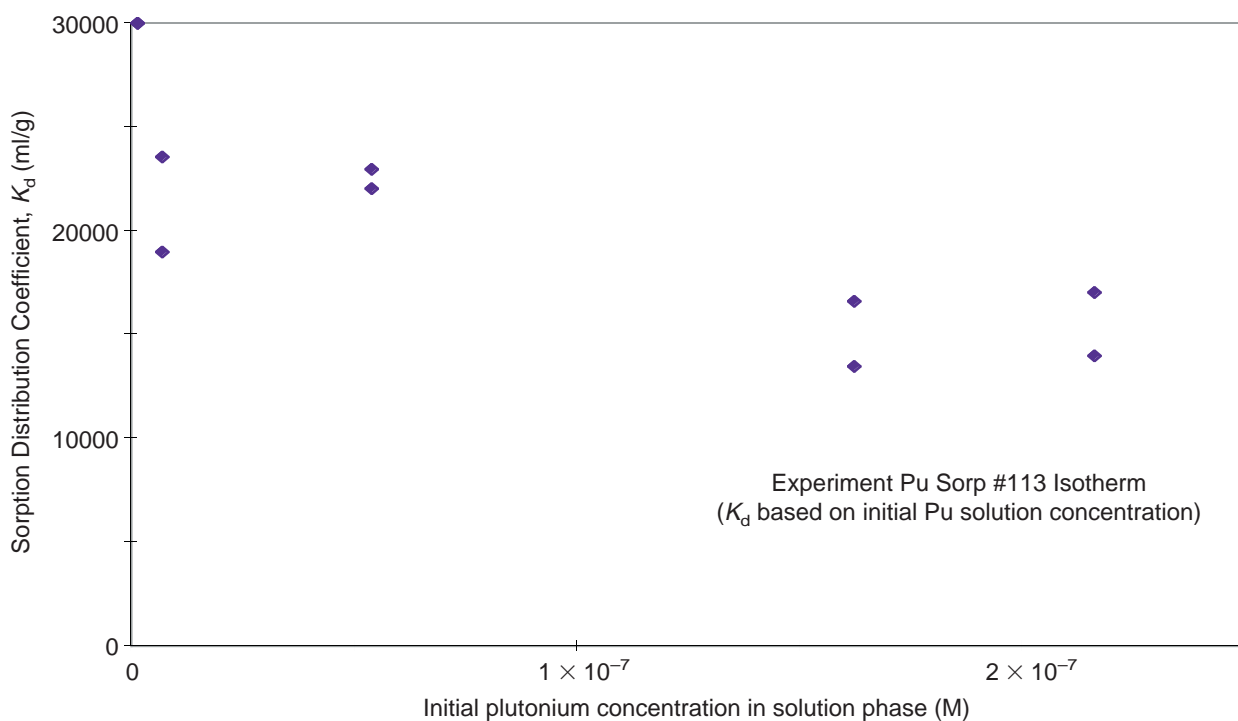


Figure 43. Plutonium Isotherm for Montmorillonite in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption distribution coefficients (diamonds) for sorption onto montmorillonite under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

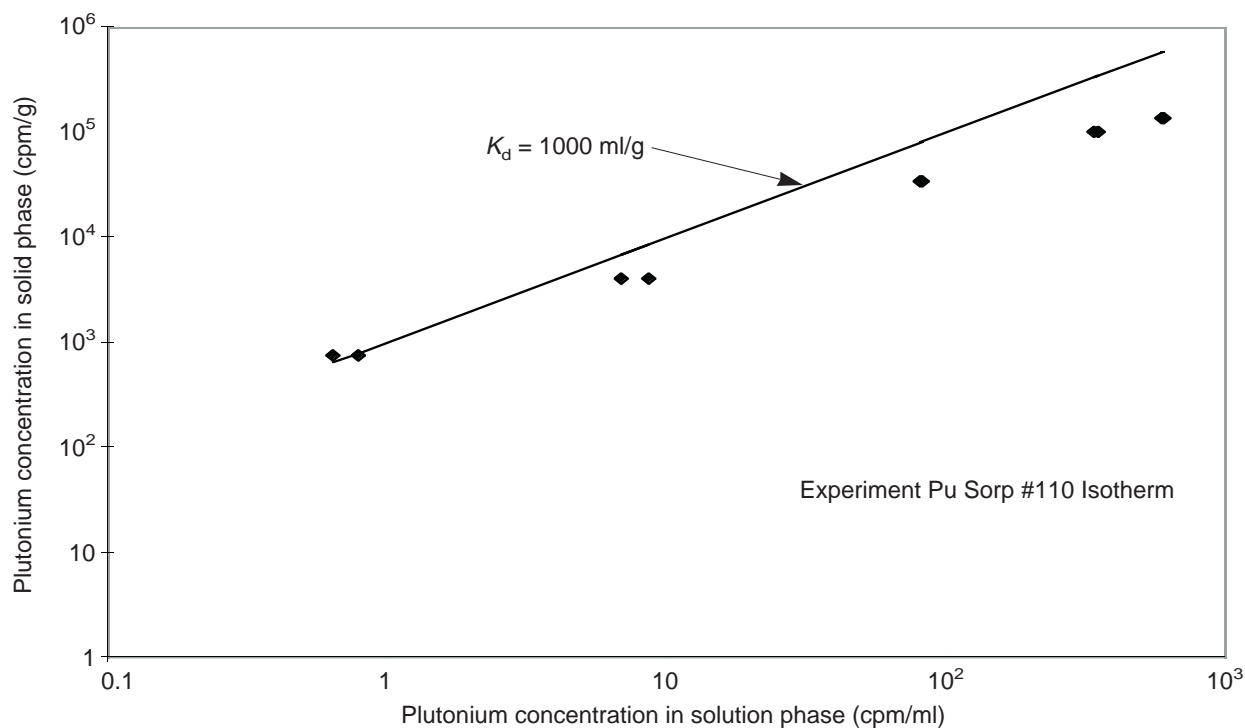


Figure 44. Plutonium Isotherm for Natural Calcite in J-13 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto natural calcite under atmospheric conditions in J-13 well water. The period of sorption was 21 days.

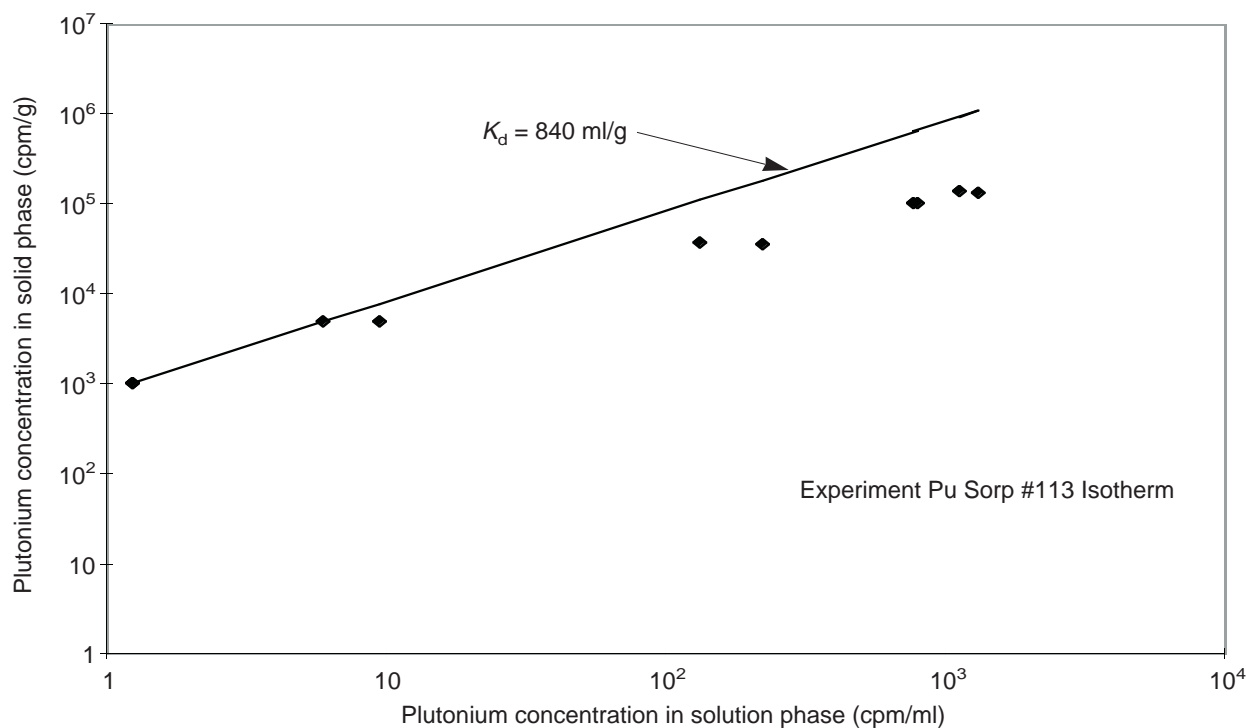


Figure 45. Plutonium Isotherm for Natural Calcite in Synthetic UE-25 p#1 Water. This plot shows plutonium sorption data (diamonds) and a linear isotherm (line) for sorption onto natural calcite under atmospheric conditions in synthetic UE-25 p#1 water. The period of sorption was 21 days.

continued from page 73

Qualitative evidence for behavior in the surficial environment.

The literature on the behavior of cesium, radium, and strontium in the surficial environment is voluminous and will not be reviewed here. Their sorption behavior is fairly well understood and is largely controlled by ion-exchange reactions (Bolt and Bruggenwert 1976), although surface-complexation reactions involving these elements have also been discussed (for example, Balistrieri and Murray 1982). The dominant controls on the ion-exchange reactions are the cation-exchange capacities of the minerals in the system, the abundances of these ion-exchanging minerals, their selectivity coefficients for the various cations in the solution phase, and the concentrations of the competing cations in the solution phase. The selectivity of most clays and zeolites for cesium, radium, and strontium is greater than the selectivities for the major cations in solution. Further, pH does not have a significant effect on the sorption behavior of these elements over the pH range of interest. Because their sorption behavior is fairly well understood and because this behavior depends strongly on local conditions, data from sites other than Yucca Mountain will not be reviewed here.

Data from laboratory sorption experiments.

Sorption coefficients for cesium, radium, and strontium were reviewed by Daniels et al. (1983), Thomas (1987), and Meijer (1990). For cesium at low concentrations (10^{-8} M), sorption coefficients are greater than 100 ml/g for all water-rock combinations tested except UE-25 p#1 water in contact with vitric tuff (Knight and Thomas 1987). Cesium sorption coefficients for the devitrified-tuff/J-13-water system show a clear concentration dependence that has been modeled with a Freundlich isotherm (Polzer and Fuentes 1988). The coefficients for this particular rock-water system are greater than 100 ml/g for cesium solution concentrations below 5×10^{-5} M. For UE-25 p#1 water in contact with this rock type, the coefficient would be 100 ml/g at somewhat lower solution concentrations. In any case, in the higher ionic-strength waters (0.02 eq/l), including unsaturated-

zone waters, the sorption coefficients for cesium on devitrified and vitric samples may be less than 100 ml/g if solution concentrations of cesium exceed 10^{-6} M. For zeolitic tuffs, cesium sorption coefficients are greater than 100 ml/g for all water compositions and cesium concentrations anticipated in the potential repository environment.

Radium appears to have a somewhat higher affinity for sorption onto Yucca Mountain tuffs than cesium. In addition, the solubility of RaSO_4 limits the concentrations in solution to trace levels (10^{-7} – 10^{-8} M; Ogard and Kerrisk 1984). At concentrations below the solubility limit for RaSO_4 , sorption coefficients for radium are greater than 100 ml/g in essentially all rock-water combinations tested, using barium as an analog for radium (Knight and Thomas 1987). This fact suggests that a minimum sorption coefficient of 100 ml/g can be used for radium in all rock-water systems. For zeolitic samples, minimum values of 1,000 ml/g can be used.

Strontium sorption behavior is more sensitive to mineral and water compositions than the other two elements discussed in this section. For devitrified and vitric tuffs, sorption coefficients for the higher ionic-strength waters (such as UE-25 p#1) are in the range of 10 to 30 ml/g (Knight and Thomas 1987). These sorption coefficients will decrease as the solution concentration of strontium is increased above approximately 10^{-5} M (Thomas 1987). However, this concentration is close to the solubility limit for SrCO_3 in these waters so that the 1000 ml/g range is likely appropriate for use in performance-assessment calculations in the devitrified or vitric tuffs. For zeolitic tuffs, a minimum value of 1,000 ml/g would be appropriate (Knight and Thomas 1987).

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The existing sorption-coefficient database for cesium, radium, and strontium should be adequate for performance-assessment calculations. The main concern would be the concentration of

cesium in the solution phase in contact with devitrified and vitric tuffs. If this concentration is over 10^{-5} M, the appropriate value for the sorption coefficient may be less than the minimum recommended value of 100 ml/g. The sorption coefficients for strontium in devitrified and vitric tuffs will be as low as 10 to 30 ml/g in higher ionic-strength waters. If additional experiments were to be carried out for this group of elements, they should focus on strontium in contact with devitrified and vitric tuffs in the higher ionic-strength waters.

Nickel and Lead

Behavior in solutions representative of Yucca Mountain groundwaters.

The aqueous solution behavior of nickel and lead is relatively simple. Within the range of groundwater compositions expected in the Yucca Mountain flow system, these elements are present in solution primarily as simple divalent cations. Several per cent of the total nickel concentration will be present as the $\text{NiSO}_4^+(\text{aq})$ complex. Similarly, several per cent of the total lead concentration will be present as the PbCl^+ complex.

Qualitative evidence for behavior in the surficial environment.

The behavior of nickel and lead in the surficial environment has been studied in some detail (for example, Snodgrass 1980). These elements are generally quite particle-reactive. The dominant mechanisms that control their sorption behavior are ion exchange on clay minerals (for example, Bowman and O'Connor 1982) and adsorption onto various oxides (for example, Theis and Richter 1980). The selectivities of clay minerals for nickel and lead are large relative to the major cations (such as Mg^{2+}) in typical groundwaters (Decarreau 1985; Bolt et al. 1983). Solution compositional parameters that can influence this adsorption behavior include pH, ionic strength, concentrations of competing ions, and concentrations of complexing agents (see review by Rai and Zachara 1984).

Data from laboratory sorption experiments.

Data on the sorption behavior of nickel in Yucca Mountain rock-water systems were reported by Knight and Lawrence (1988). Sorption and desorption ratios were determined in several water compositions in the pH range from 8.3 to 9.0 with nickel concentrations in solution of approximately 10^{-8} M. For devitrified and zeolitic samples, sorption coefficients were in the range of 200 to 400 ml/g. Sorption coefficients obtained in the desorption step were generally a factor of two larger than the sorption coefficients. In the only vitric sample analyzed, sorption coefficients ranged from approximately 30 to 70 ml/g. For the desorption step, the coefficients were in the range of 33 to 72 ml/g for this rock type. We were unable to find references to the adsorption behavior of lead on tuffaceous or even granitic rock samples.

Data on sorption of transition metals on synthetic zeolites suggest that Pb^{2+} has a high affinity for ion exchange compared with Sr^{2+} , whereas Ni^{2+} has a lower affinity relative to Sr^{2+} (Barrer and Townsend 1976; Obeng et al. 1981; Blanchard et al. 1984). This suggests the zeolitic zones within Yucca Mountain could be significant barriers to lead migration.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

Based on information in the literature, the sorption behavior of these elements will be determined largely by the free-ion activities in solution and the cation-exchange capacity of the host rock (for example, Bowman and O'Connor 1982 and Rai and Zachara 1984). Solution pH and oxide-mineral abundances may be a factor in rocks in which nickel and lead sorb primarily by surface-complexation mechanisms. In any case, lead appears to sorb more strongly than nickel in most surficial environments, and both elements appear to sorb more strongly than strontium (Bowman and O'Connor 1982). The nickel sorption coefficients discussed in the previous section could reasonably be used as default values for lead in performance-assessment calculations. For nickel, a minimum

sorption coefficient of 100 ml/g could be used in the devitrified and zeolitic zones. For the vitric zones, the performance-assessment calculations could be done using random sampling and a normal distribution ranging from 0 to 50 ml/g.

Neptunium, Protactinium, Selenium, and Uranium

The main factor that neptunium, protactinium, selenium, and uranium have in common is that they all tend to show small values for sorption coefficients in the rock-water systems expected within Yucca Mountain under oxidizing conditions. Under more reducing conditions, they would all have much lower solubilities and higher sorption affinities in Yucca Mountain groundwaters. As the solution and sorption behavior is somewhat different for each of these elements, they will be discussed separately.

Neptunium

Behavior in solutions representative of Yucca Mountain groundwaters.

In solutions representative of water compositions expected within the Yucca Mountain flow system, neptunium will be predominantly in a +5 oxidation state. Unlike pentavalent niobium and protactinium, Np(V) compounds are relatively soluble (Nitsche et al. 1994). This result appears to be due to the formation of the oxocation NpO_2^+ in solution. Pentavalent niobium and protactinium apparently do not form analogous oxocations (that is, NbO_2^+ and PaO_2^+) in near-neutral solutions to an appreciable degree. Instead they hydrolyze and form insoluble precipitates. The NpO_2^+ ion appears to be quite stable in aqueous solutions (Cotton and Wilkinson 1988).

Nitsche et al. (1992, 1994) studied the solubilities and speciation of neptunyl compounds in solutions representative of water compositions expected within Yucca Mountain. The results at 25°C and several pH values are summarized in Table 14. The solubility-controlling solids were found to be hydrated sodium neptunyl carbonates, and the pri-

mary species for the water compositions expected at Yucca Mountain were NpO_2^+ and $\text{NpO}_2(\text{CO}_3)^-$. The speciation results of Table 14 for J-13 water are similar, although not identical, to those calculated using the EQ3 speciation code (Nitsche 1991).

At higher temperatures (60° and 90°C), neptunium was less complexed by carbonate at pH values of 6 and 7 but more highly complexed with carbonate at a pH of 8.5. The solubilities at 60°C were similar to those in Table 14, although they were somewhat higher at a pH of 8.5 relative to the 25°C results.

Qualitative evidence for behavior in the surficial environment.

Although ^{237}Np has been detected in the surficial environment (for example, Sakanoue 1987), essentially no information has been found on its transport behavior in this environment.

Data from laboratory sorption experiments.

Laboratory experiments have been carried out on neptunium sorption with a variety of rock and mineral types and solution compositions. The results of neptunium sorption experiments with pure mineral separates have been reported by Allard (1982), Meijer et al. (1989), Triay et al. (1993b), and others. On the basis of these results, it is evident that neptunium has a high affinity for ferric oxides and

Table 14. Solubility and Speciation of Neptunium in Groundwaters at 25°C

Water	pH	Solubility (M)	NpO_2^+	$\text{NpO}_2\text{CO}_3^-$
J-13	6	5×10^{-3}	90%	10%
	7	1×10^{-4}	45%	55%
	8.5	4×10^{-5}	40%	60%
UE-25 p#1	6	3×10^{-3}	100%	0%
	7	5×10^{-4}	60%	40%
	8.5	7×10^{-6}	0%	100%

oxyhydroxides, apatite, and attapulgite (a magnesium-rich clay). It has a somewhat lower affinity for carbonates (such as calcite), sulfates (for example, anhydrite) and manganese minerals (for example, cryptomelane). It has a low affinity for most silicate minerals. Neptunium also shows high affinities for minerals that contain ferrous iron (such as pyrite, olivine, augite, magnetite, hornblende, epidote, biotite, and chlorite). This affinity is likely due to the reduction of Np^{5+} to Np^{4+} by Fe^{2+} on the surfaces of these minerals. Although ferrous iron-bearing minerals are, at best, minor species in Yucca Mountain tuffs (Bish and Chipera 1989), they could be of considerable significance to neptunium sorption.

In addition to the nature of the available mineral surfaces, it is also evident that pH is a critical parameter. In general, neptunium sorption increases with increasing pH. This effect is particularly evident in the experiments with iron oxyhydroxides (for example, Combes et al. 1992). However, similar behavior is evident in the sorption experiments with silicate minerals. In the latter case, the sorption edge (as a function of pH) is located at a higher pH (8–9) than the edge associated with the ferric oxyhydroxides (a pH of 6–7). Data reported by Combes et al. (1992) suggest neptunium is sorbed as an inner-layer complex on ferric oxyhydroxide.

Neptunium does not appear to have a high affinity for ion-exchange reactions on clays and zeolites (Allard 1982; Triay et al. 1993b). This phenomenon may be due to the small charge-to-radius ratio and the large size of the neptunyl ion.

The results of neptunium sorption experiments involving Yucca Mountain rock and water samples have been reported by Daniels et al. (1982), Thomas (1987, 1988), Triay et al. (1993b), and others. These experiments indicate that neptunium has a low affinity (for example, K_d values of 0–5 ml/g) for the surfaces in Yucca Mountain tuffs over most of the pH range and water compositions expected in the Yucca Mountain flow system. The sorption mechanisms are apparently not entirely

reversible as coefficients obtained from desorption experiments are commonly larger than those obtained from sorption experiments even though the isotherms are linear in the concentration range covered by these experiments. There is some indication of increased sorption coefficients (5–40 ml/g) at the highest pH values (8.5–9.0).

Torstenfelt et al. (1988) suggest that this result reflects increased hydrolysis of the neptunyl ion, resulting in an increase in surface-adsorption reactions. However, in Yucca Mountain rock-water systems, it could also reflect increased potential for calcite precipitation at high pH.

In the pH range from 6.5 to 8.5, the small but consistent affinity of neptunium for the tuffs most likely reflects the existence of a limited number of favorable adsorption sites for neptunium. This number apparently does not involve ion-exchange sites because zeolitic rock samples also show low sorption coefficients. For example, Thomas (1988) describes a case in which a zeolitic tuff sample (G4-1608) with a cation-exchange capacity of approximately 1.5 meq/g appears to have essentially the same affinity for neptunium as a devitrified tuff sample (GU3-433) with an exchange capacity of approximately 0.02 meq/g. These sites are apparently not present in the same abundance on all tuff samples. That is, some zeolitic, vitric, and devitrified tuff samples have almost no affinity for neptunium over the pH range from 6.5 to 8.5, whereas other samples with similar proportions of major minerals show sorption coefficients in the range of 5 to 10 ml/g. This result suggests, but does not prove, that the favorable sites are associated with some minor primary or secondary phase that has variable abundance. Hematite and calcite are candidates for this phase based on pure mineral studies. Because ferric oxides are present at trace levels in most of the rock units within Yucca Mountain, they could be the source of the low but consistent values (0.5–2 ml/g) observed in experiments on devitrified and zeolitic tuffs. Alternatively, neptunium may be sorbed (through reduction to Np^{4+}) by the small amounts of ferrous-iron-bearing minerals present in the rock samples used

in the sorption experiments.

The increased sorption of neptunium on tuffaceous samples known to contain calcite suggests this mineral is of considerable potential significance to neptunium sorption on Yucca Mountain tuffs. If so, prediction of the adsorption behavior of neptunium will depend on knowledge of the surface areas of calcite in the various hydrologic units or on the saturation state of calcite in groundwaters present in these units. Because even small amounts of calcite appear to significantly increase neptunium sorption coefficients, current mineral identification techniques may not be adequate for prediction of neptunium sorption behavior. A more viable approach may be to determine the calcite saturation level in the various groundwater compositions expected within Yucca Mountain. If calcite is saturated or oversaturated in a given groundwater, the upper end of the range of experimentally determined sorption coefficients could be used with the assumption that neptunium will either coprecipitate with calcite or adsorb to calcite surfaces. Alternatively, if calcite is undersaturated in a given water, the lower end of the range could be used under the assumption that neptunium is sorbed on oxides, such as ferric or ferrous oxides. For vitric units lacking iron oxides and calcite, neptunium may not be sorbed at all.

We studied the sorption of Np(V) onto samples of the three types of tuff in J-13 water (under oxidizing conditions) at two pH values (7 and 8.5). However, to identify the sorbing minerals in the tuffs, we also studied sorption onto the pure minerals hematite, clinoptilolite, albite, and quartz. We found that neptunium in J-13 water does not sorb onto devitrified and vitric tuffs, albite, and quartz (Table 15).

The initial neptunium concentrations for the data reported in Table 15 ranged from 1×10^{-7} to 3×10^{-5} M. We used wet-sieved tuffs, albite, and quartz samples with particle sizes in the range from 75 to 500 μm . The pretreatment period lasted 2 to 3 days, and the sorption period, 2 to 4 days. The

Table 15. Neptunium Sorption in J-13 Water under Oxidizing Conditions

Solid phase	pH	K_d (ml/g)*
G4-268, devitrified tuff	7	7×10^{-3}
	8.5	-4×10^{-2}
GU3-1405, vitric tuff	7	2×10^{-1}
	8.5	3×10^{-1}
Quartz	7	-1×10^{-1}
	8.5	-2×10^{-1}
Albite	7	-8×10^{-2}
	8.5	-1×10^{-1}

*The uncertainties in the data are ± 0.5

negative values reported in the table are a result of the analytical error for the case of very little sorption (that is, a small number is obtained as the difference of two large numbers).

For the experimental conditions cited earlier, the sorption of neptunium onto zeolitic tuffs and clinoptilolite appears to be linear in the concentration range from 1×10^{-7} to 3×10^{-5} M and can be fitted using a K_d (Figs. 46 and 47). The sorption of neptunium onto zeolites is higher at a pH of 7 than a pH of 8.5, which might be explained by the larger amount of NpO_2^+ relative to $\text{NpO}_2\text{CO}_3^-$ in J-13 water at a pH value of 7 than at a pH value of 8.5.

One surprise for neptunium is the relatively small amount of sorption (values of K_d ranging from 1.5 to 3 ml/g) compared to the large amount expected for a cation-exchange sorption mechanism in a zeolite with a large cation-exchange capacity (such as clinoptilolite). This result indicates that the sorption mechanism for neptunium onto clinoptilolite is a surface reaction rather than cation exchange within the cages of the zeolite. One possible explanation is steric: the shape and large size of the neptunyl cation prevents cation exchange. This ion likely has a trans-dioxol configuration normal to a puckered equatorial ring containing six bound water molecules.

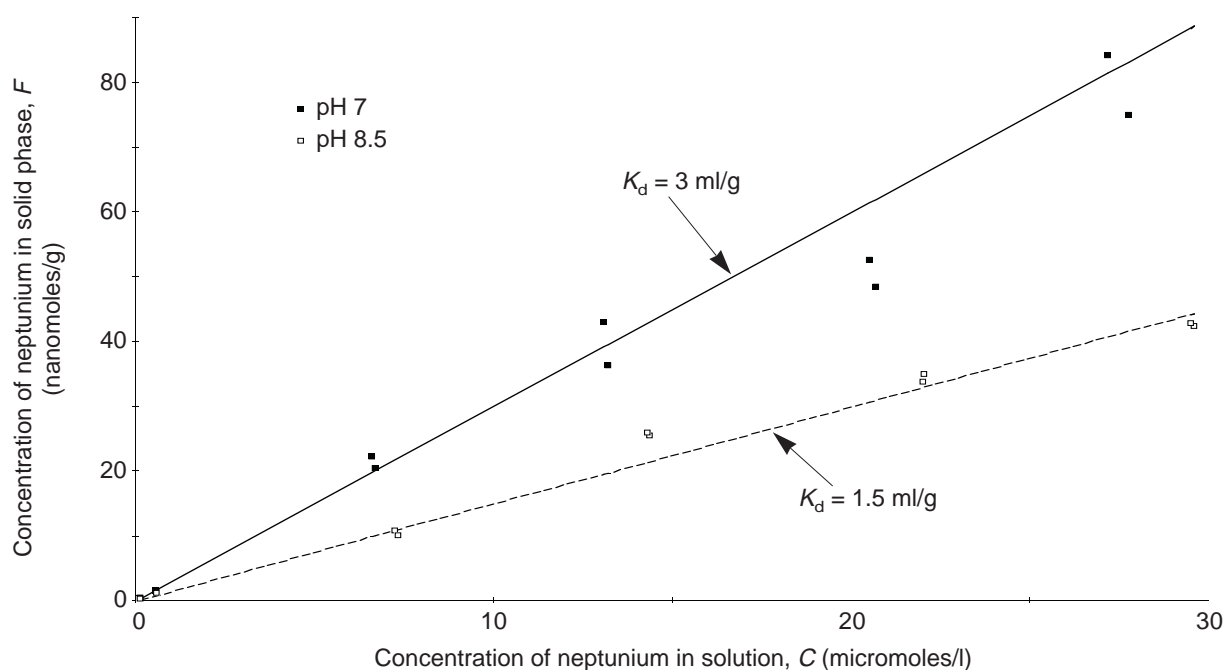


Figure 46. Neptunium Sorption onto Clinoptilolite-rich Tuff. A plot is shown of the concentration, F , of neptunium in the solid phase of the clinoptilolite-rich tuff G4-1510 versus the concentration, C , of neptunium in the solution phase of J-13 well water and linear (K_d) fits to the data for two values of pH.

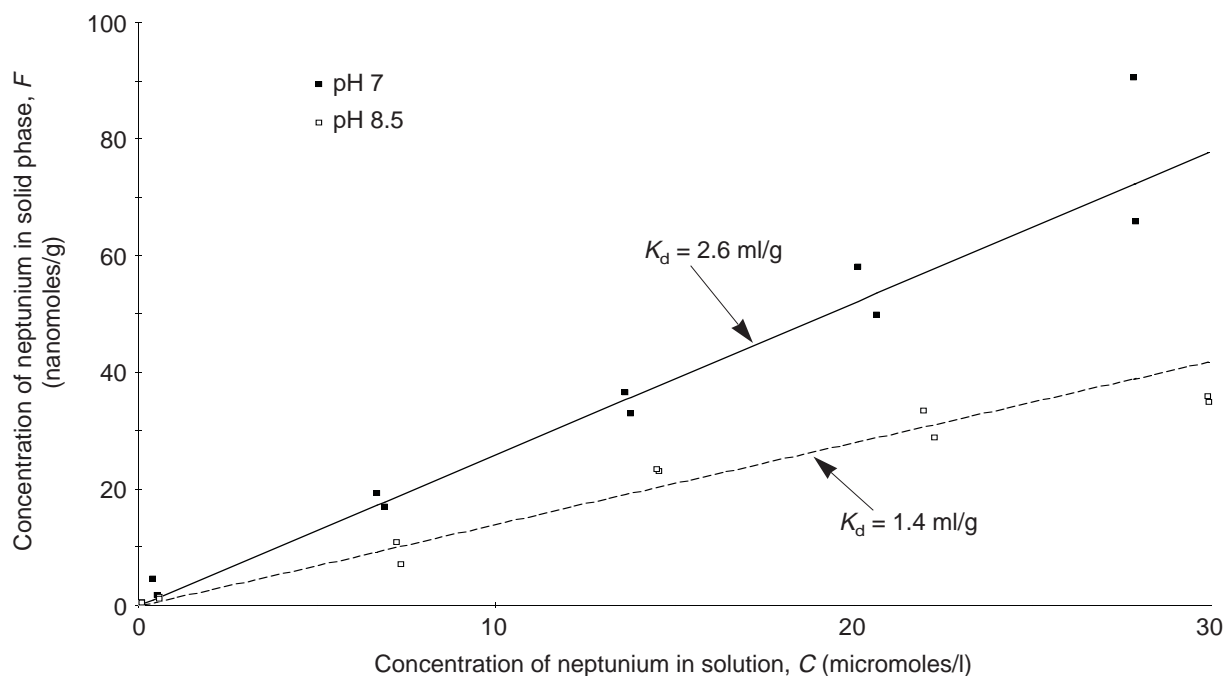


Figure 47. Neptunium Sorption onto Clinoptilolite. A plot is shown of the concentration, F , of neptunium in the solid phase of clinoptilolite versus the concentration, C , of neptunium in the solution phase of J-13 well water and linear (K_d) fits to the data for two values of pH.

The experiments with pure clinoptilolite indicate that sorption increases with decreasing pH for Np(V). Because the major constituent of tuff G4-1510 is clinoptilolite, predictions of the K_a (K_d divided by the solid-phase surface

area) were made for neptunium sorption onto this tuff by assuming that clinoptilolite is the only sorbing phase. Table 16 shows measured and predicted values of K_a for the clinoptilolite-rich tuff G4-1510 at two different pH values. Because sorption is correlated with surface area, we made similar calculations (Table 17) for a series of tuff samples containing various amounts of clinoptilolite for which the surface area had been measured. The values in the two tables indicate that reasonable predictions can be made based on neptunium sorption data for pure clinoptilolite (assuming clinoptilolite is the only sorptive mineral).

Table 16. Prediction of Neptunium Sorption on Clinoptilolite-rich G4-1510 Tuff in J-13 Water

Initial concentration (M)	pH	Measured K_a (m)	Predicted K_a (m)*
1×10^{-7} to 3×10^{-5}	7	1×10^{-7}	9×10^{-8}
	8.5	6×10^{-8}	5×10^{-8}

*Assuming clinoptilolite is the only sorbing mineral in the tuff

The sorption of neptunium onto pure iron oxides is very large (we measured values of K_d for hematite that range from 100 to 2000). Although the sorption onto pure hematite is very large, neptunium sorption onto devitrified tuffs, which appear to have traces of hematite ($1\% \pm 1$), is essentially zero. This result could be due to differences in the surface of pure hematite compared to hematite in tuff. It could also be due to passivation of the hematite surfaces in the tuff by elements (such as the rare earths) that have a higher affinity for hematite than neptunium and, thus, occupy the sorption sites.

Table 17: Neptunium Sorption onto Clinoptilolite-rich Tuffs in J-13 Water*

Tuff sample	Measured K_a (m)	Predicted K_a (m)	Clinoptilolite percentage
G1-1405	1×10^{-7}	1×10^{-7}	68 ± 7
G4-1505	9×10^{-8}	1×10^{-7}	74 ± 7
G4-1506	1×10^{-7}	1×10^{-7}	62 ± 7
G4-1510	8×10^{-8}	1×10^{-7}	59 ± 7
G4-1529	7×10^{-8}	1×10^{-7}	59 ± 8
G4-1625	9×10^{-8}	1×10^{-7}	61 ± 7
G4-1772	1×10^{-7}	1×10^{-7}	63 ± 5
G4-2077	5×10^{-8}	8×10^{-8}	51 ± 8

*Atmospheric conditions; initial neptunium concentrations ranged from 6 to 8×10^{-7} M; tuffs were wet-sieved to particle sizes ranging from 75 to 500 μm ; the pretreatment period was 2 to 14 days; and the sorption period was 3 to 23 days.

We investigated sorption as a function of sieving procedure for devitrified (G4-270) and zeolitic (G4-1506) tuffs in J-13 and UE-25 p#1 well waters. Data presented in Fig. 48 indicate that wet-sieving probably eliminates small particles that cause artificially high K_d values. As previously determined by Rogers and Chipera (1994), the optimal batch-sorption procedure involves wet-sieving the tuff samples to a size of 75 to 500 μm . Figure 49 illustrates the problem that could arise when sorption experiments are performed with pure minerals consisting of very finely divided particles that cannot be wet-sieved. The neptunium batch-sorption coefficients determined vary by more than an order of magnitude between the dry- and the wet-sieved natural calcite. The potential differences in surface area and particle size between a pure mineral and that same mineral in the tuff samples may make predictions of sorption behavior on whole rock impossible when the basis of those predictions is pure mineral work. As illustrated in Fig. 49, the trends in sorption as a func-

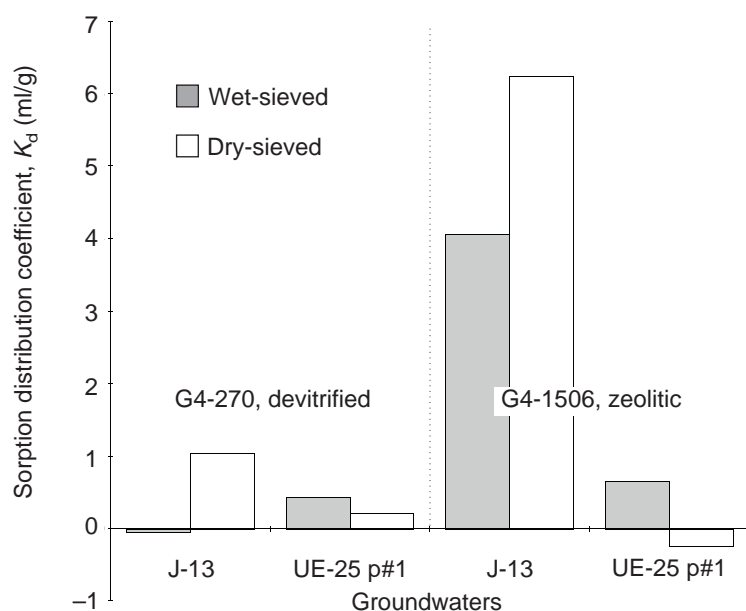


Figure 48. Neptunium Sorption for Wet- and Dry-sieved Tuffs.

Experimental values of the batch-sorption distribution coefficient, K_d , are shown for sorption of neptunium onto tuff (under atmospheric conditions) that allow comparisons of both groundwaters (J-13 and UE-25 p#1), two types of tuff (devitrified and zeolitic), and wet- or dry-sieving to particle sizes ranging from 75 to 500 μm . The initial neptunium concentration was 1×10^{-6} M. The pretreatment period with the two groundwaters was 13 to 15 days; the neptunium sorption period was 21 to 22 days.

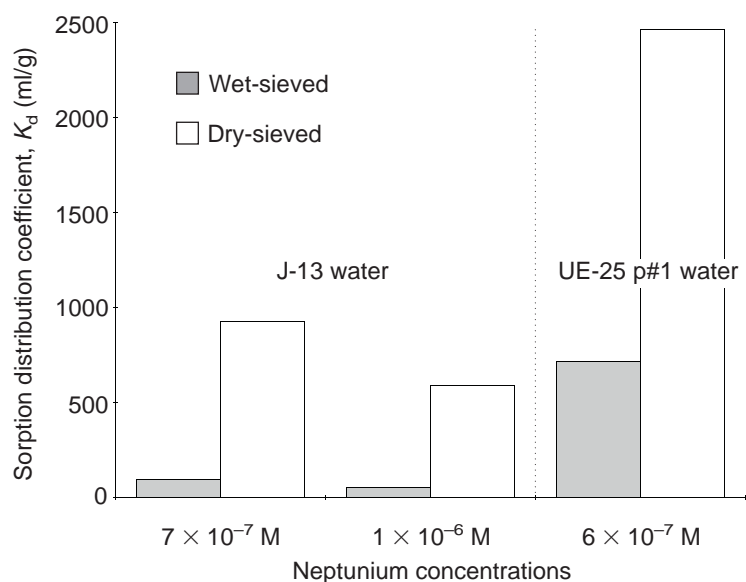


Figure 49. Neptunium Sorption for Wet- and Dry-sieved Calcite.

Experimental values of the batch-sorption distribution coefficient, K_d , are given for sorption of neptunium onto calcite (under atmospheric conditions) that allow comparisons of both groundwaters (J-13 and UE-25 p#1), different initial concentrations of neptunium, and wet- or dry-sieving to particle sizes ranging from 75 to 500 μm . The pretreatment period was 14 to 15 days; the sorption period was 17 to 24 days.

tion of concentration and groundwater chemistry stay the same regardless of whether dry- or wet-sieved calcite is used.

Consequently, the most effective use of pure mineral sorption data is the identification of trends in the sorptive behavior of a mineral. Figures 48 and 49 also illustrate the effect of water chemistry on neptunium sorption; for example, the sorption of neptunium onto zeolitic tuffs decreases consider-

ably with the increasing carbonate content and ionic strength of the UE-25 p#1 water. The reverse trend is observed for calcite samples.

We investigated the kinetics of neptunium sorption onto tuffs and pure minerals and found that the sorption of neptunium onto tuffs and clinoptilolite appears to be fast (Fig. 50). No significant differences are observed in neptunium sorption as a function of time for the tuffs studied and for

clinoptilolite. This is not the case for pure minerals that tend to sorb by means of a coprecipitation mechanism (such as calcite) or by surface complexation (such as hematite). Figures 51 and 52 show the sorption dependence on time for calcite and hematite in waters from the Wells J-13 and UE-25 p#1. The dissolution/precipitation reactions that may accompany the coprecipitation of neptunium with calcite may be slow compared with other sorption mechanisms. Future experiments will address this issue by monitoring the chemistry of the groundwater as it is being equilibrated with these minerals.

Figures 53 and 54 give further data from our investigation of the dependence of neptunium sorption on pH in J-13 water. The figures show that for vitric tuffs (such as samples G2-767 and GU3-1407), pH does not seem to make a significant difference in the amount of neptunium sorption measured. Likewise, the sorption of neptunium onto devitri-

fied tuffs (such as sample G4-270) in J-13 is not affected by pH. Samples G2-1813, G2-1951, G2-2000, and G2-2222 are zeolitic tuffs, but until the XRD analyses of these samples become available, it is difficult to know the relative amounts of clinoptilolite versus mordenite in each. However, tuff samples G4-1510 and G4-1395 consist of 59% and 22% clinoptilolite, respectively, and exhibit the same trend as clinoptilolite itself: an increase in sorption as the pH is decreased from 8.5 to 7, probably because of the increase of neptunyl cation concentration. As discussed earlier, these results seem to indicate that neptunium sorption onto clinoptilolite may follow an ion-exchange mechanism, but the fact that neptunium sorption on pure clinoptilolite is so small favors a surface-complexation reaction, even for this zeolite. Again, the reason may be that the hydrated neptunyl cation is too large to fit in the zeolite cages.

We also studied the sorption of neptunium in

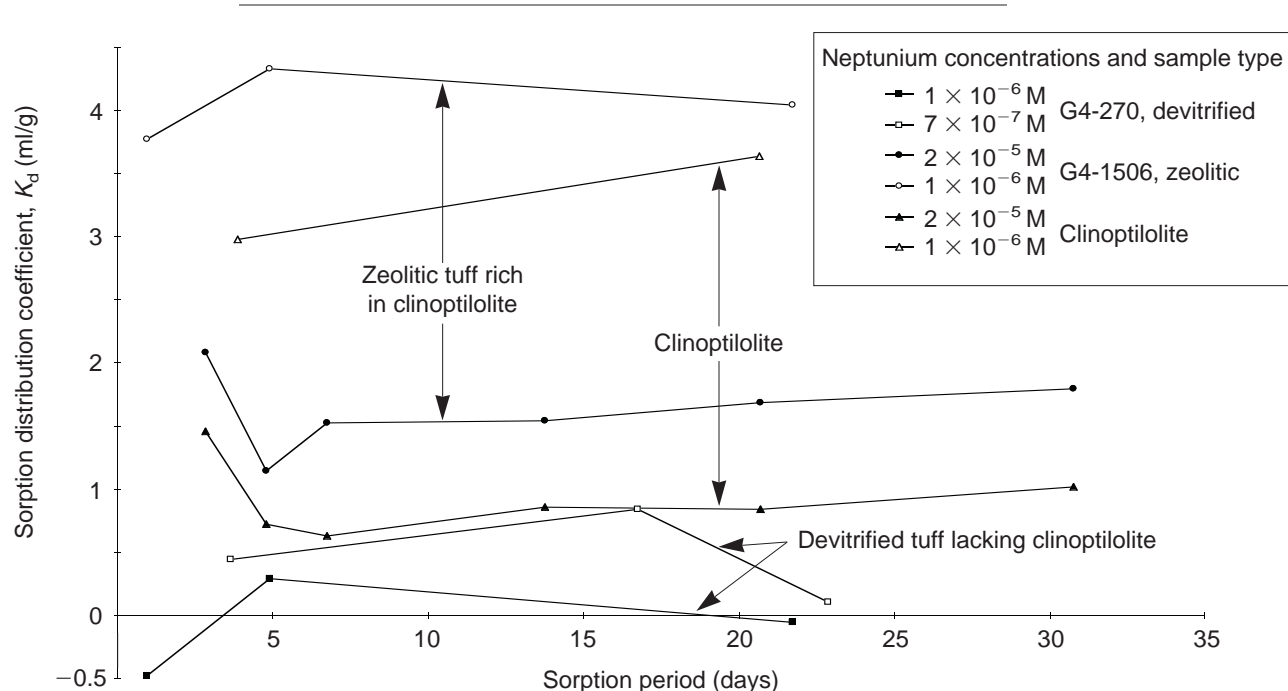


Figure 50. Time Dependence of Neptunium Sorption for Tuffs and Clinoptilolite. Variation with time of K_d for sorption of neptunium onto devitrified tuff (G4-270) lacking clinoptilolite (squares), zeolitic tuff (G4-1506) rich in clinoptilolite (circles), and pure clinoptilolite (triangles) under atmospheric conditions and at the specified initial neptunium concentrations in J-13 well water. Tuffs were wet-sieved to particle sizes from 75 to 500 μ m; the clinoptilolite was not sieved. The pretreatment period was 2 to 14 days.

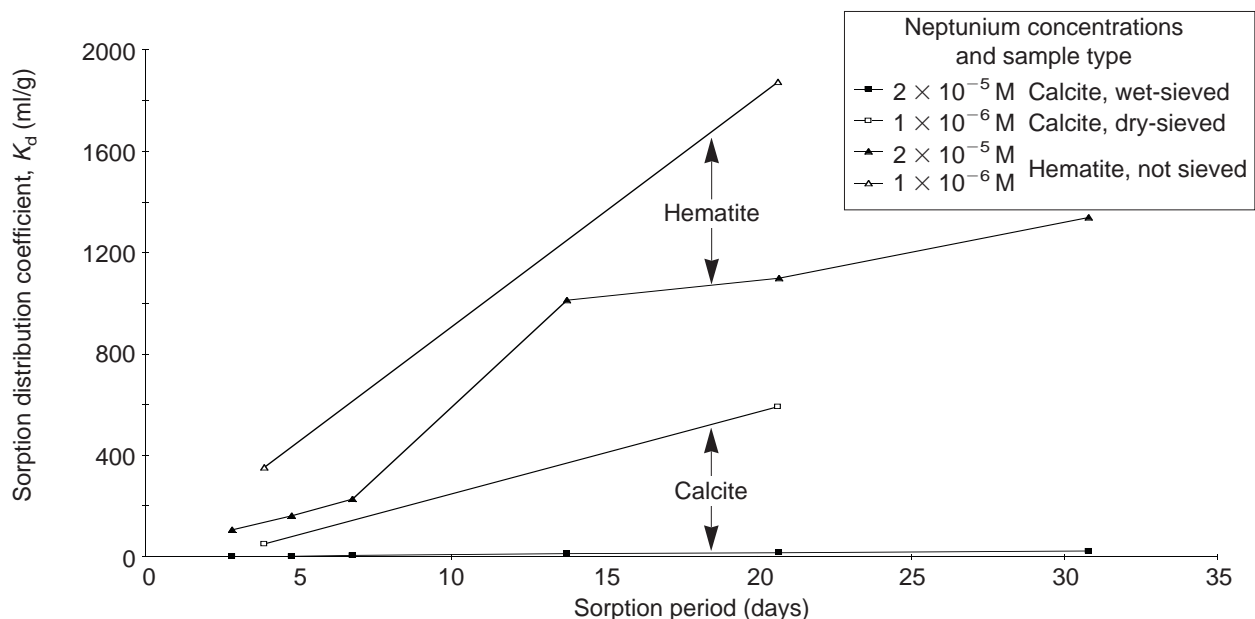


Figure 51. Time Dependence of Neptunium Sorption for Calcite and Hematite in J-13 Water.

Variation with time of K_d for sorption of neptunium onto calcite (squares) and hematite (triangles) under atmospheric conditions and at the specified initial neptunium concentrations in J-13 well water. The calcite was either wet- or dry-sieved to particle sizes from 75 to 500 μm ; the synthetic hematite was not sieved. The pretreatment period with J-13 water was 2 to 14 days.

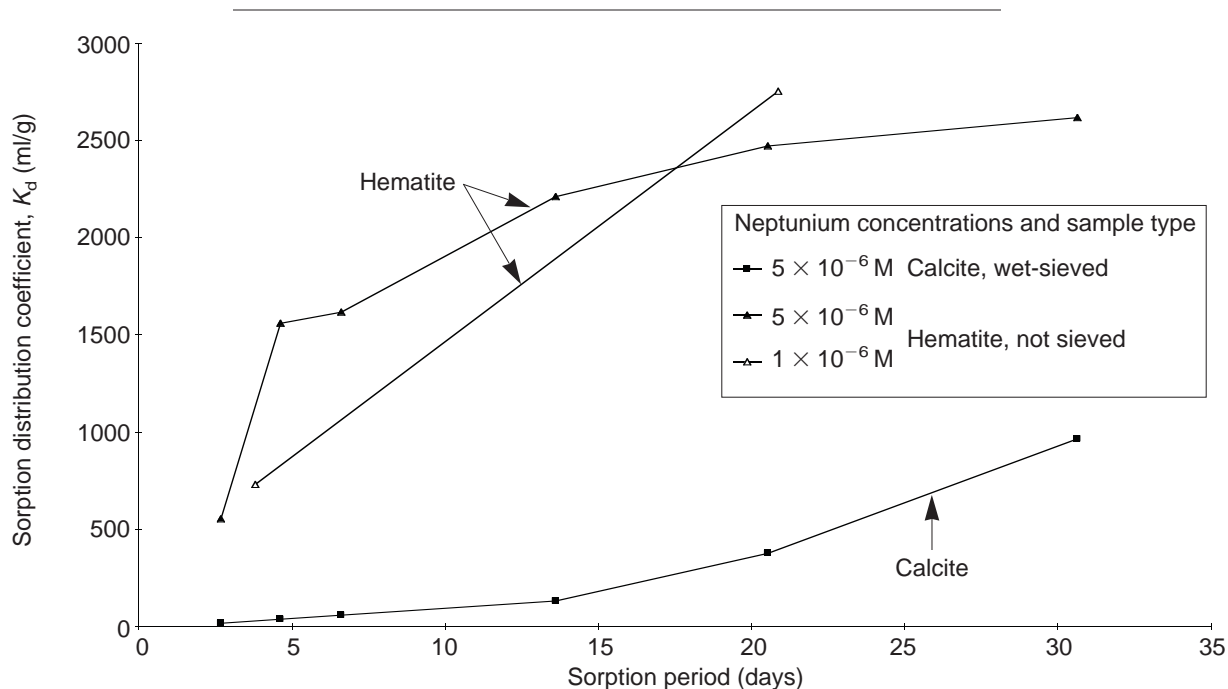


Figure 52. Time Dependence of Neptunium Sorption for Calcite and Hematite in UE-25 p#1 Water.

Variation with time of K_d for the sorption of neptunium onto calcite (squares) and hematite (triangles) under atmospheric conditions and at the specified initial neptunium concentrations in UE-25 p#1 well water. The calcite was wet-sieved to particle sizes ranging from 75 to 500 μm ; the synthetic hematite was not sieved. The pretreatment period in UE-25 p#1 water was 2 to 13 days.

UE-25 p#1 water and found that, regardless of the conditions, neptunium sorption onto tuffs and zeolites is negligible ($K_d < 1$ ml/g) in this water (Fig. 55). If clinoptilolite is the only mineral affecting neptunium sorption and if ion exchange at the surface is the dominating mechanism, one might conclude that the reason for the lack of neptunium sorption on clinoptilolite is the formation of the neptunium carbonate complex ($\text{NpO}_2\text{CO}_3^-$) in UE-25 p#1 water to the exclusion of the neptunyl cation. The data reported by Nitsche et al. (1994) do not support this conclusion (Table 14); the relative amount of neptunyl in UE-25 p#1 water is larger than that in J-13 water at a pH of 7. If the data of Nitsche et al. are correct, another possible reason for the lack of neptunium sorption on clinoptilolite in UE-25 p#1 water is competitive effects due to the larger ionic strength of that water compared with J-13 water, which has a smaller ionic strength by nearly an order of magnitude.

As we mentioned earlier, iron oxides have a high affinity for neptunium (Combes et al. 1992). Figure 56 shows further data on the sorption of

neptunium onto hematite, this time in both J-13 and UE-25 p#1 waters as a function of pH. It is important to note that the trends observed in this figure (sorption increasing with increasing pH and larger sorption in UE-25 p#1 water than in J-13 water) are not followed by the neptunium sorption reported for clinoptilolite-rich tuff samples. Also once again, the neptunium sorption in the rest of the tuff samples is so small (even in the samples that contain traces of hematite) that the iron oxides appear to be passivated in the tuffs.

As illustrated in Fig. 57, regardless of the tuff studied, neptunium sorption onto tuffaceous materials is extremely limited. One exception is tuff sample G2-723 (not shown), which contains a large amount of calcite, a good sorber for neptunium. This sample will be discussed later.

Figure 58 is a plot both of neptunium sorption data in J-13 water and of surface area for tuffs for which BET-surface-area and XRD analyses exist. The surface-area data correspond to the surface area for the tuffs sieved in J-13 water with the following

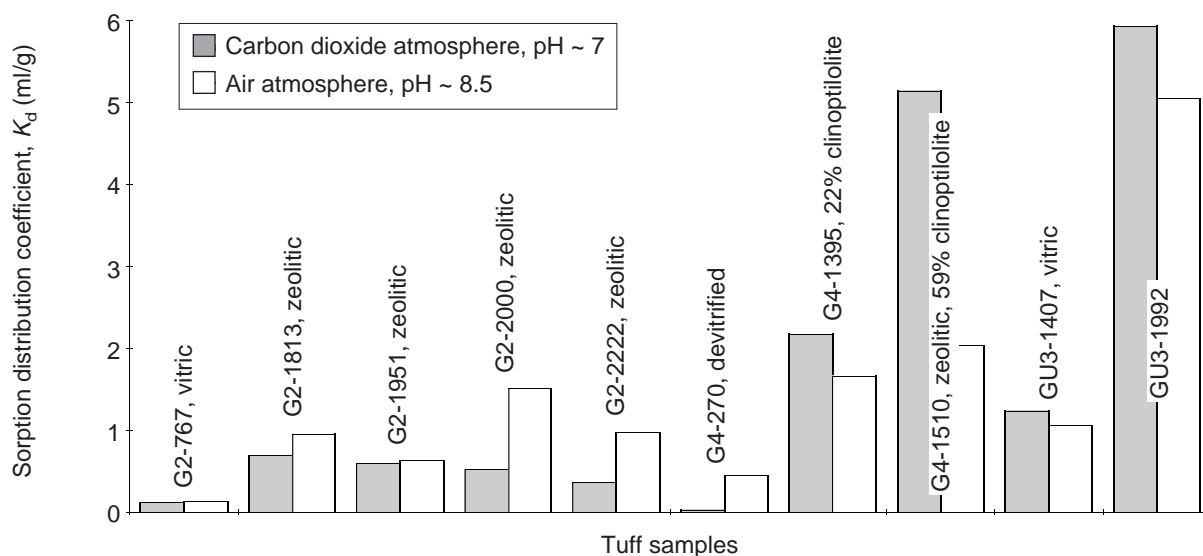


Figure 53. pH Dependence of Sorption at 10^{-7} M. Experimental values of K_d for the sorption of neptunium onto tuffs in J-13 water at initial concentrations of 6 to 7×10^{-7} M are compared for atmospheric conditions (pH ~ 7) and a carbon-dioxide overpressure (pH ~ 8.5). Tuffs were wet-sieved to particle sizes from 75 to 500 μm . The pretreatment period was 2 to 3 days; the sorption period was 3 to 5 days.

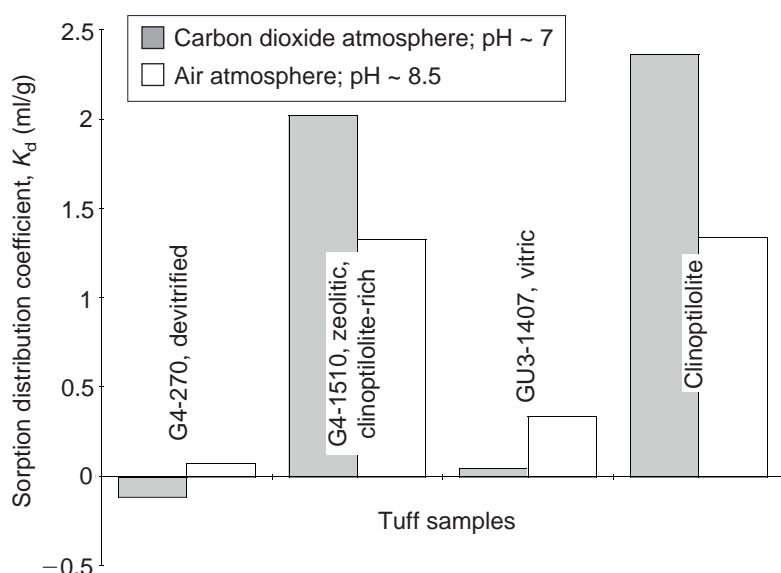


Figure 54. pH Dependence of Sorption at 10^{-5} M. Experimental values of K_d for the sorption of neptunium onto several tuffs and clinoptilolite in J-13 well water at an initial neptunium concentration of 3×10^{-5} M are compared for both atmospheric conditions (pH ~ 8.5) and a carbon-dioxide overpressure (pH ~ 7). Tuffs were wet-sieved to particle sizes that ranged from 75 to 500 μ m; the clinoptilolite was not sieved. The pretreatment period was 2 to 3 days; the sorption period was 3 to 5 days.

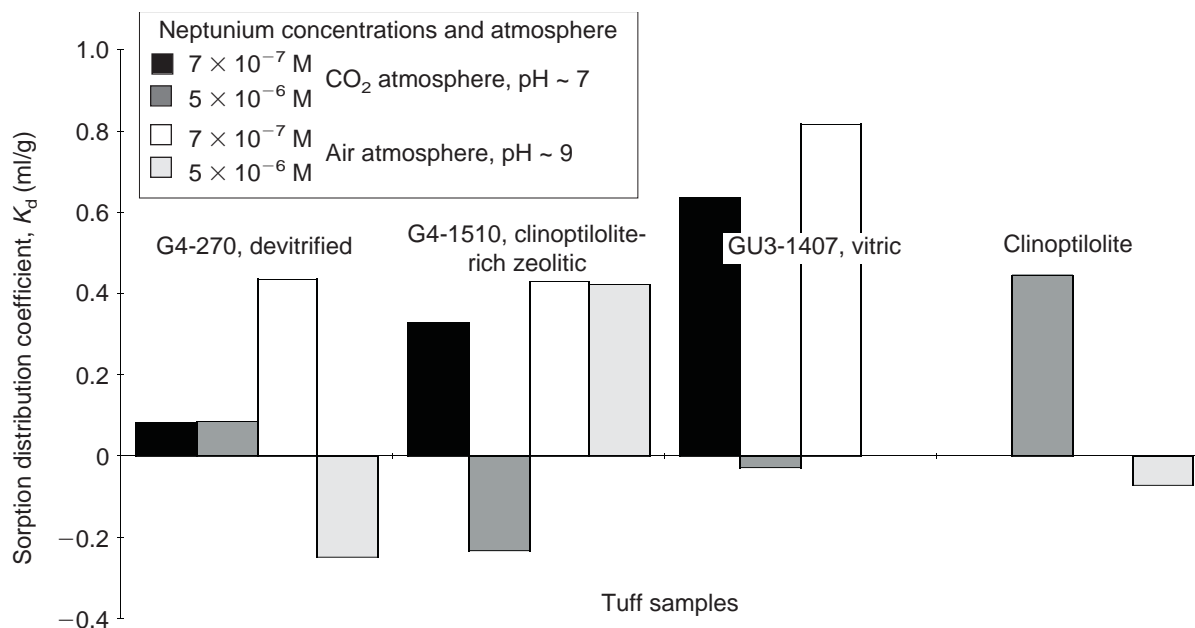


Figure 55. Neptunium Sorption in UE-25 p#1 Well Water. Experimental values of the batch-sorption distribution coefficient, K_d , for neptunium in UE-25 p#1 water show negligible sorption regardless of sample type (devitrified tuff, clinoptilolite-rich zeolitic tuff, vitric tuff, or clinoptilolite), pH (~ 7 or ~ 9), or initial neptunium concentration (5×10^{-6} or 7×10^{-7}).

exceptions: the surface area used for sample G4-2077 was for dry-sieved tuff; the surface area used for tuffs G4-268 and G4-272 was the same as that measured for tuff G4-270; the surface area plotted for tuffs G4-1505 and G4-1510 was the

same as that measured for tuff G4-1506; and the surface area plotted for tuff GU3-1405 was the same as that measured for tuff GU3-1407. Figure 58 shows a reasonable correlation between sorption and surface area. The surface areas that are

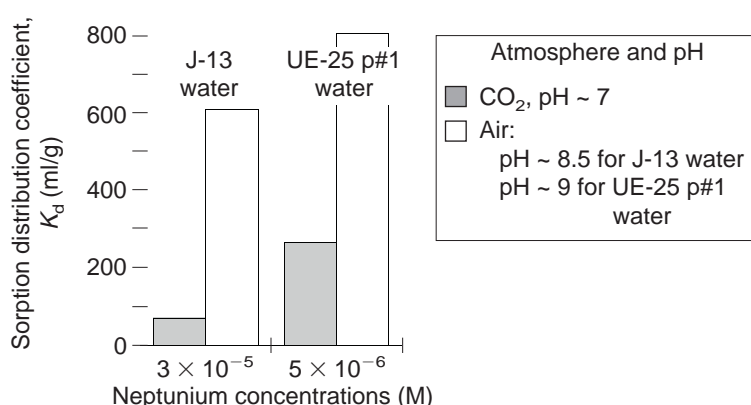


Figure 56. Neptunium Sorption for Hematite. Values of the batch-sorption distribution coefficient, K_d , are given for the sorption of neptunium onto hematite in UE-25 p#1 well water at the specified initial neptunium concentrations and pH values. The pretreatment period was 2 to 3 days, and the sorption period was 3 to 5 days.

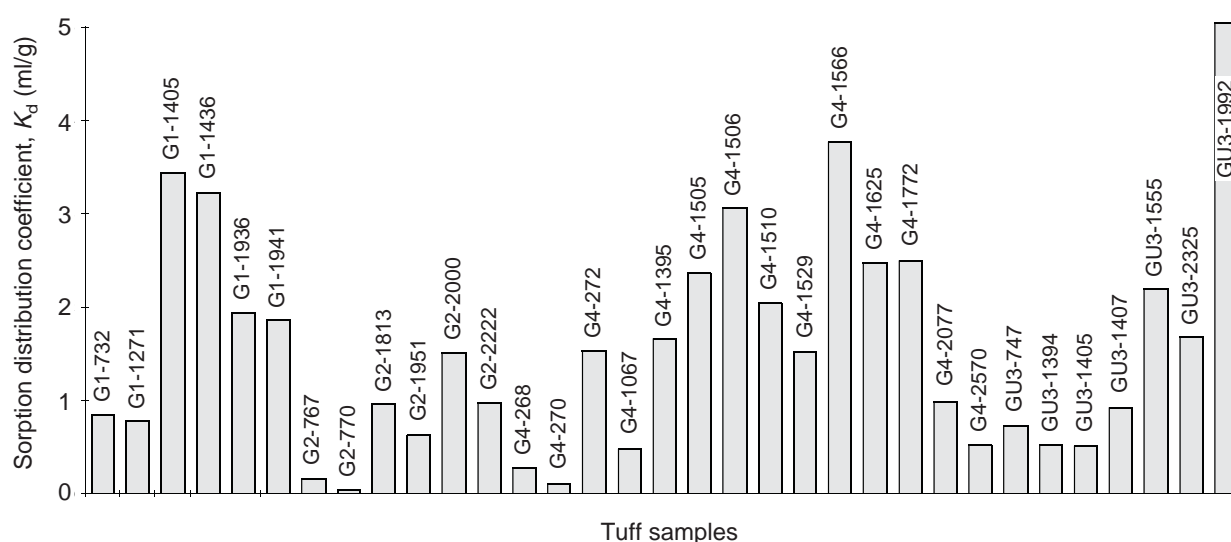


Figure 57. Neptunium Sorption in J-13 Well Water. These values of the batch-sorption distribution coefficient, K_d , illustrate the limited sorption of neptunium onto a large range of Yucca Mountain tuffs in J-13 well water under atmospheric conditions. The initial neptunium concentration ranged from 6 to 8×10^{-7} M. The tuffs were wet-sieved to particle sizes that ranged from 75 to 500 μ m. The pretreatment period was 2 to 14 days; the sorption period was 3 to 23 days.

larger than 18 m²/g correspond to clinoptilolite-rich tuffs.

Figures 59 and 60 summarize the sorption of neptunium under atmospheric conditions for tuffs and minerals as a function of water type. Sorption onto zeolitic tuffs decreases considerably with increasing carbonate content and ionic strength of the water. Figure 60 also shows the calcite-rich tuff G2-723 (34% calcite), which exhibits considerable sorptive capacity for neptunium. Assuming that

the calcite in the tuff sample has the same surface area as the natural calcite used for these experiments (and that calcite is the only sorptive mineral in the tuff), one would predict from neptunium sorption on pure calcite a $\log(K_d)$ for tuff G2-723 of 1.5. This prediction agrees well with the measured K_d (Fig. 60).

As the neptunium concentration is increased towards the solubility limit for neptunium in the J-13 and UE-25 p#1 groundwaters, the observed

sorption decreases, but the general trends remain the same (as seen by comparing Figs. 58 and 61). The extremely low neptunium sorption reported for devitrified tuffs in J-13 and UE-25 p#1 waters is supported by the sorption data plotted for albite (Fig. 62), which appears to be a very poor sorber for neptunium (in both waters). The nonlinearity of neptunium sorption in the high-concentration region (approaching the solubility limits for neptunium) is further illustrated in Figs. 63 and 64 (for J-13 and UE-25 p#1 waters under a carbon-dioxide atmosphere at a pH of 7).

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The mechanisms by which neptunium appears to sorb onto mineral surfaces in the Yucca Mountain flow system appear to be surface complexation on oxide phases and coprecipitation and surface

adsorption involving carbonate minerals. The surface-complexation mechanism appears to be relatively insensitive to variations in ionic strength, detailed groundwater composition, and pH over the range from 6.5 to 8.5. This mechanism is likely responsible for the 0.5 to 5.0 ml/g range in sorption-coefficient values consistently measured in many different rock samples. The high end of this range may reflect secondary mechanisms, such as the reduction of Np(V) to Np(IV) on mineral surfaces containing ferrous iron. Regardless of the details of the mechanisms, performance-assessment calculations could use a probability distribution for sorption-coefficient values, as was done for the 1993 total-system performance assessment (Wilson et al. 1994).

For hydrologic units in which calcite is known to be present or in which groundwaters are oversatu-

continued on page 100

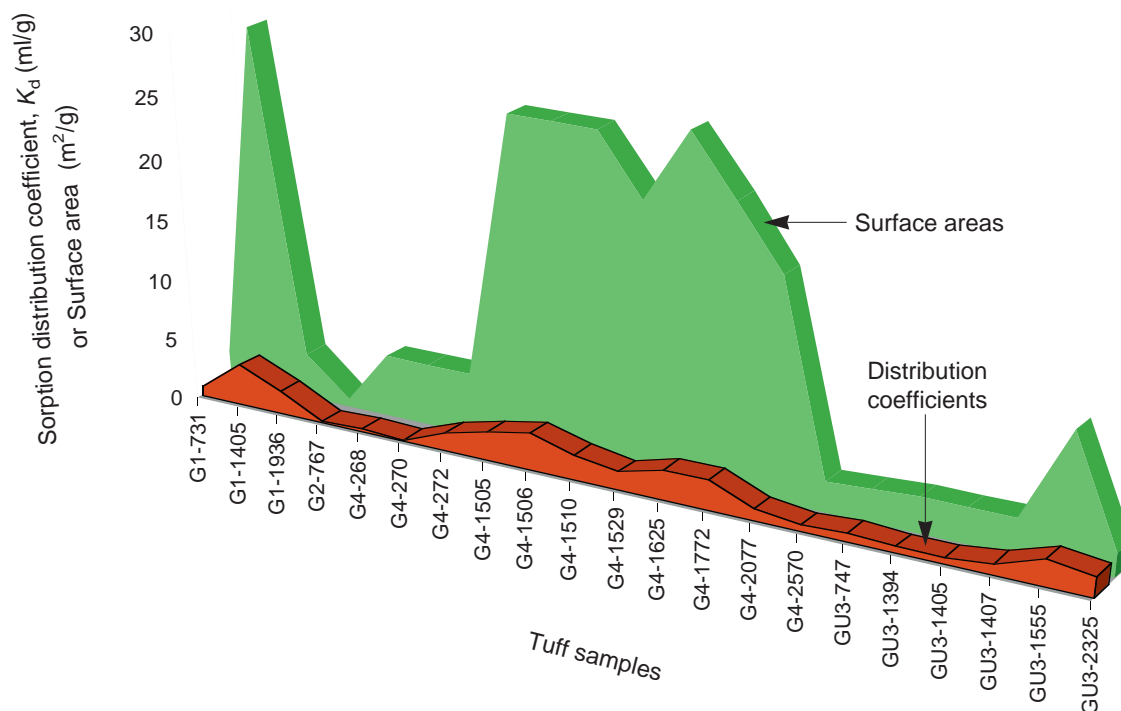


Figure 58. Neptunium Sorption and Surface Area. Values of the batch-sorption distribution coefficient, K_d , for neptunium onto various tuffs are compared to the corresponding surface areas of those tuffs. The sorption is for J-13 well water under atmospheric conditions at an initial neptunium concentration ranging from 6×10^{-7} to 8×10^{-7} M. The tuffs were wet-sieved to particle sizes that ranged from 75 to 500 μm . The pretreatment period was 2 to 14 days; the sorption period was 3 to 23 days.

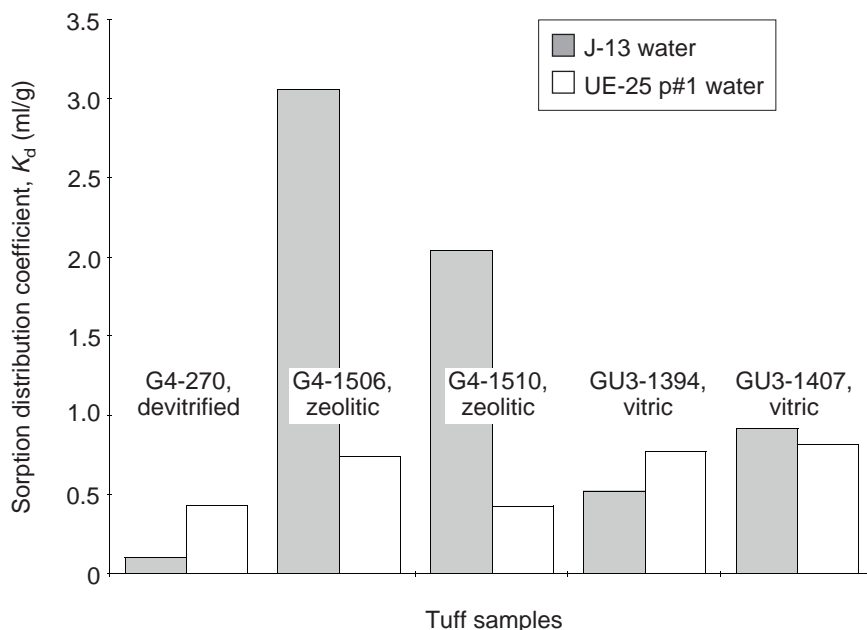


Figure 59. Dependence on Water for Sorption onto Tuffs. Values of K_d for sorption of neptunium onto several tuffs that allow comparison of sorption (under atmospheric conditions) for the two types of groundwaters. The initial neptunium concentration ranged from 6×10^{-7} to 8×10^{-7} M. The tuffs were wet-sieved to particle sizes ranging from 75 to 500 μm . The pretreatment period was 2 to 14 days, and the sorption period was 3 to 23 days.

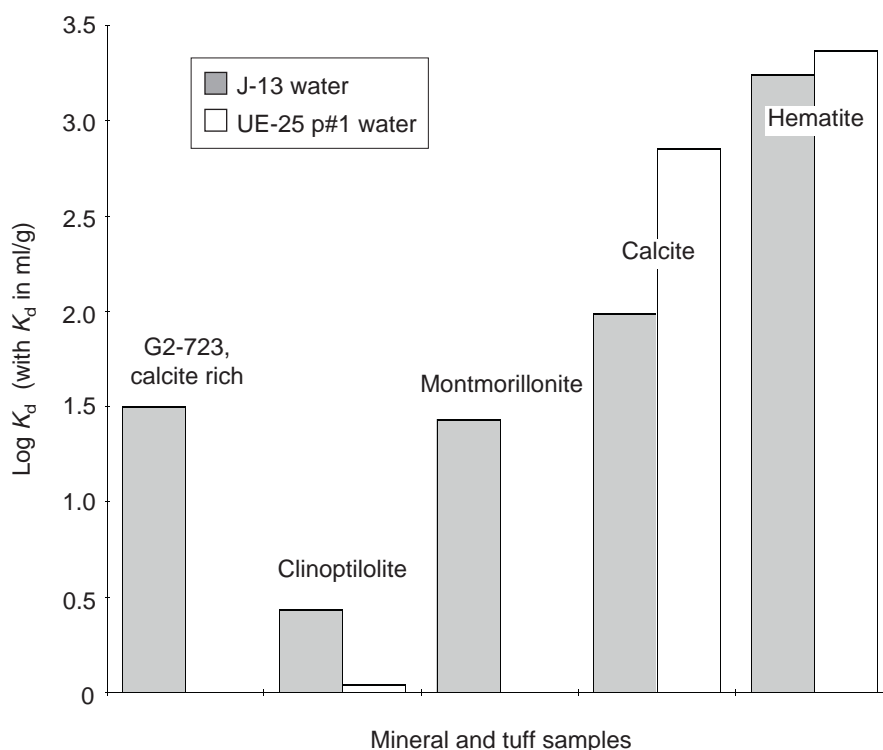


Figure 60. Dependence on Water for Sorption onto Minerals. Values of K_d for neptunium onto several minerals and a calcite-rich tuff that allow comparison of sorption (under atmospheric conditions) for the two groundwaters. The initial neptunium concentration ranged from 6×10^{-7} to 8×10^{-7} M. The tuff and the calcite were wet-sieved to particle sizes ranging from 75 to 500 μm , the montmorillonite was dry-sieved; the clinoptilolite and hematite were not sieved. The sorption period was 17 to 22 days.

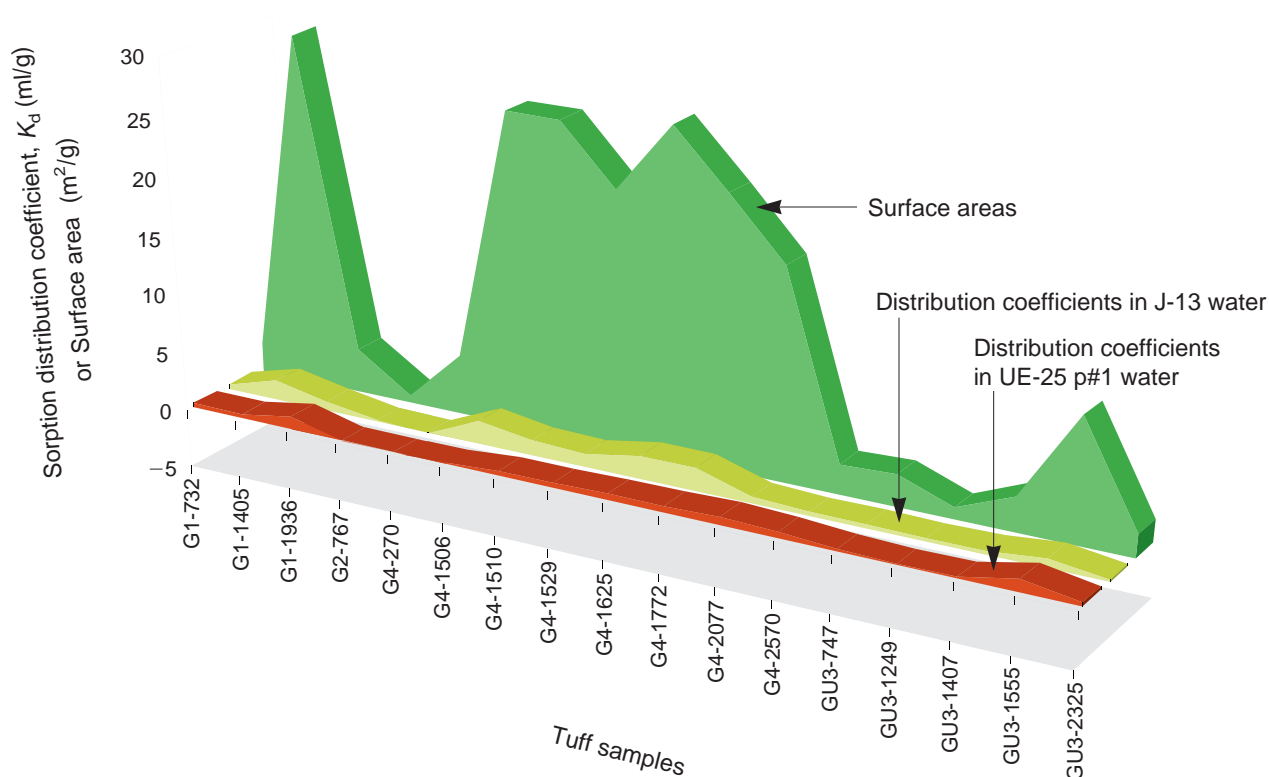


Figure 61. High-concentration Sorption onto Tuffs. Values of K_d for sorption of neptunium onto tuffs under atmospheric conditions and near the solubility limit (initial neptunium concentrations of 2 to 4×10^{-5} M in J-13 water and 5×10^{-6} M in UE-25 p#1 water) are compared with the surface areas of those tuffs. The tuffs were wet-sieved to particle sizes ranging from 75 to $500 \mu\text{m}$. The pretreatment period was 2 to 5 days; the sorption period was 2 to 4 days.

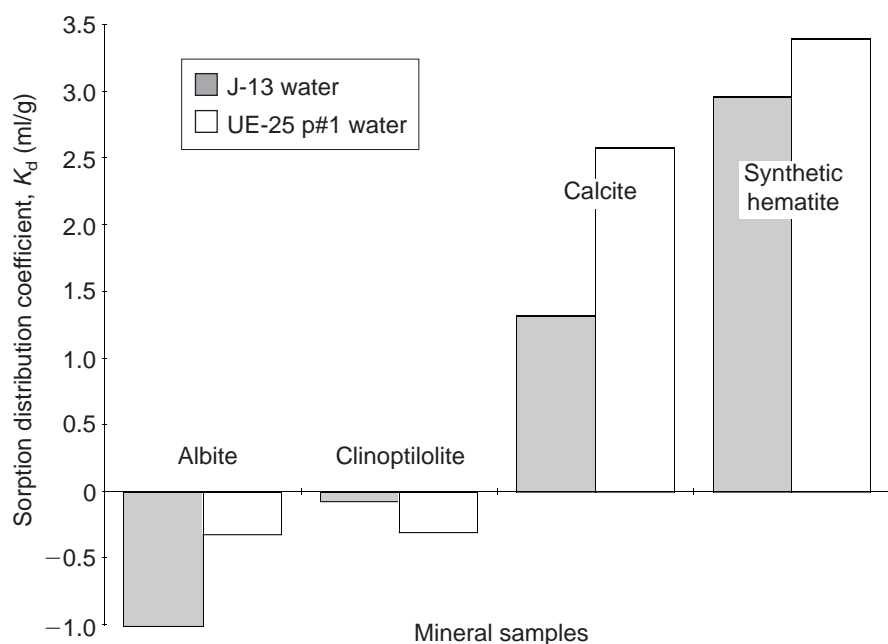


Figure 62. High-concentration Sorption onto Minerals. Values of K_d for sorption of neptunium onto minerals under atmospheric conditions for neptunium concentrations near the solubility limit (initially, 2 to 4×10^{-5} M in J-13 water and 5×10^{-6} M in UE-25 p#1 water). The calcite was wet-sieved to particle sizes ranging from 75 to $500 \mu\text{m}$; the others were not sieved. The pretreatment period was 2 to 31 days; the sorption period was 21 days.

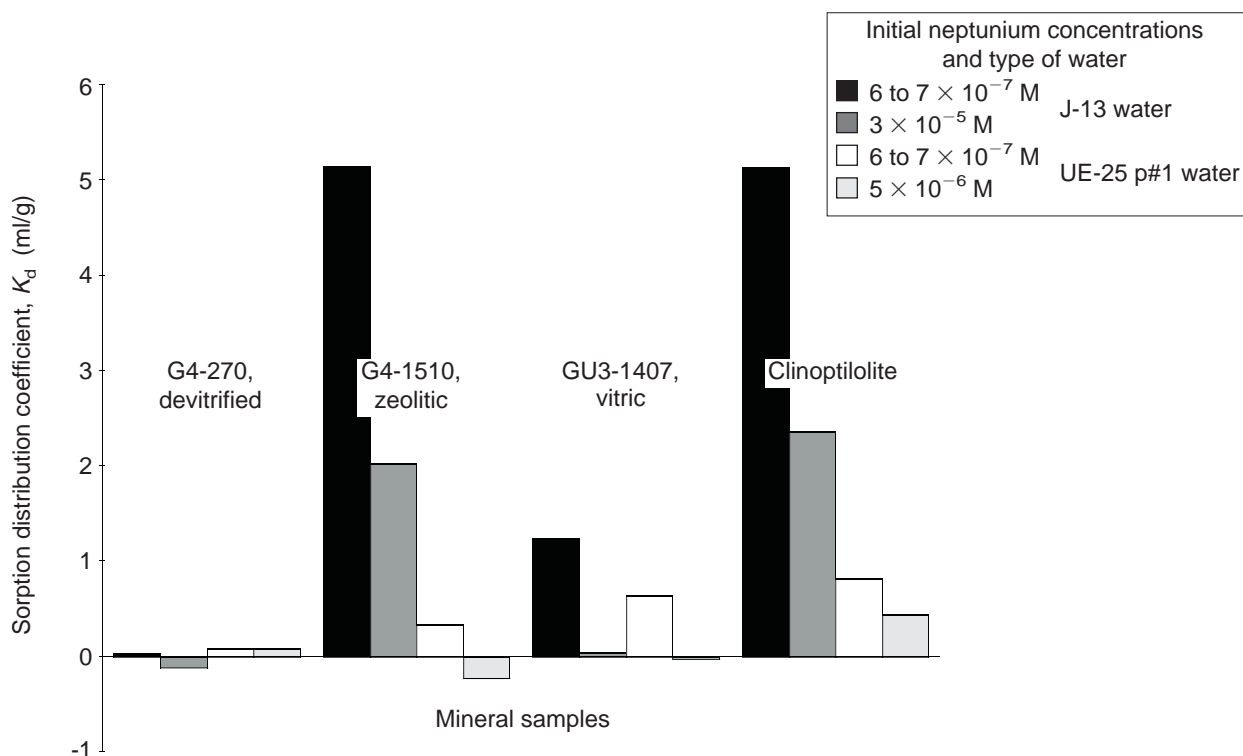


Figure 63. High-concentration Sorption onto Tuffs at pH 7. Values of K_d for sorption of neptunium onto several tuffs and clinoptilolite under a carbon-dioxide overpressure (to obtain a pH of approximately 7) are shown. The tuffs were wet-sieved to particle sizes ranging from 75 to 500 μm ; the clinoptilolite was not sieved. The pretreatment period was 2 to 3 days; the sorption period was 3 to 4 days.

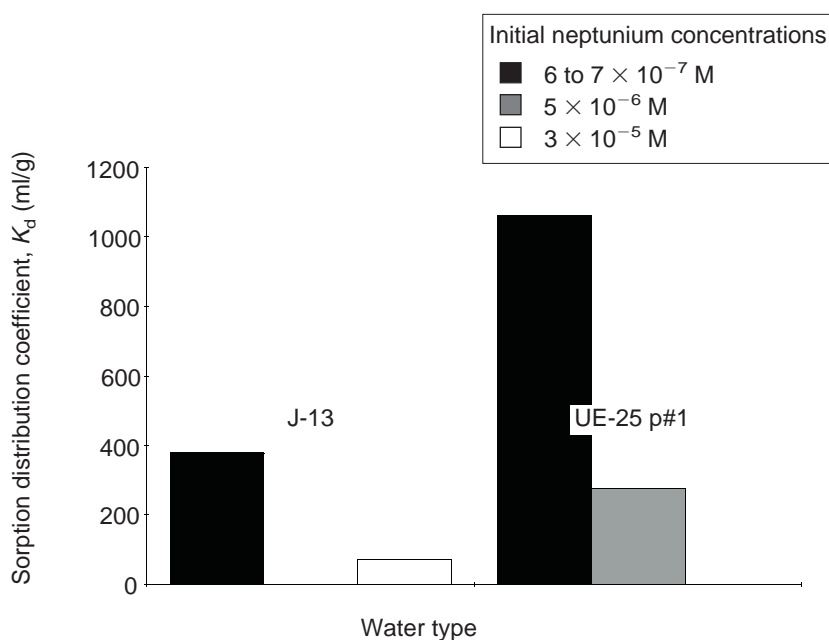


Figure 64. High-concentration Sorption onto Hematite at pH 7. Values of the batch-sorption distribution coefficient, K_d , are shown for sorption of neptunium onto unsieved synthetic hematite under a carbon-dioxide overpressure (to obtain a pH of ~ 7). The pretreatment period was 2 to 3 days; the sorption period was 3 to 4 days.

continued from page 96

rated in calcite, higher neptunium sorption coefficients could be used in the calculations if it could be established through laboratory experiments that such coefficients are appropriate. To date, most neptunium sorption coefficients have been obtained using samples from the unsaturated zone, many of which came from levels above the repository horizon. According to the mineralogic studies, calcite is more common at depths below the potential repository horizon than it is at the intermediate depths. Many of the samples used in sorption experiments to date have been obtained from intermediate depths.

Protactinium

Behavior in solutions representative of Yucca Mountain groundwaters.

In aqueous systems, protactinium appears to exist dominantly in the +5 oxidation state although the +4 state may occur in reducing environments (Brookins 1988). In both oxidation states, protactinium is strongly hydrolyzed and forms highly insoluble compounds (Cotton and Wilkinson 1988). This result implies that the +5 solution chemistry of protactinium is more akin to that of Nb(V) than to other actinides in +5 oxidation states, such as PuO_2^+ or NpO_2^+ . If this interpretation is correct, then the solution parameter of greatest importance to protactinium sorption behavior would be pH.

Qualitative evidence for behavior in the surficial environment.

Information on behavior of protactinium in the surficial environment is sparse. Because protactinium forms such insoluble compounds, it is generally assumed to be immobile in the surficial environment.

Data from laboratory sorption experiments.

Batch-sorption experiments with protactinium have yielded some interesting results. In dilute to intermediate ionic-strength solutions, Allard et al. (1983) report large values (10^4 mg/l) for the protactinium sorption coefficient on alumina and silica at pH values greater than 6 to 7 but much lower

values (90–500 ml/g) at pH values less than 7. Rundberg et al. (1985) report protactinium sorption coefficients in the range from 3.7 to 8.2 ml/g for a zeolitic tuff in contact with J-13 water spiked with 10^{-11} to 10^{-14} M protactinium at pH values of 6.3 to 6.7. Together, these data suggest that protactinium sorbs by a surface-complexation mechanism and that there is a rather steep sorption edge for protactinium as a function of pH at a pH value of approximately 7.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

Batch-sorption data for protactinium suggest that sorption coefficients for this element will be large ($> 1,000$ ml/g) at a pH value greater than 7 and small (< 10 ml/g) at lower pH values. Because protactinium sorption experiments on rock samples from Yucca Mountain have only been carried out in the low pH range, it would be prudent to carry out several experiments using a Yucca Mountain water at several pH values from 7 to 9.

Selenium

Behavior in solutions representative of Yucca Mountain groundwaters.

Selenium will occur as anionic species in all water compositions expected at Yucca Mountain. Although the two oxidation states of +4 and +6 (Howard 1977) are found for selenium in surficial waters in contact with atmospheric oxygen, the +4 state predominates under the conditions expected for groundwaters at Yucca Mountain (Howard 1977; White et al. 1991). In that state, selenium is found as the SeO_3^{2-} and HSeO_3^- selenite ions. In the +6 oxidation state, selenium occurs as the SeO_4^{2-} and HSeO_4^- selenate ions.

Qualitative evidence for behavior in the surficial environment.

Selenium behavior in the surficial environment is very closely tied to the redox potential of different parts of the near-surface environment. Under reducing conditions, selenium is immobilized as FeSe_2 at low pH (< 5) and as native selenium at higher pH (Howard 1977). The stability range for

native selenium extends nearly to surface redox conditions. When in contact with atmospheric oxygen levels, selenium is apparently stabilized as the selenite ion (SeO_3^{2-}). At higher redox potentials, selenium is oxidized to the selenate ion (SeO_4^{2-}), which appears to be more mobile in the surficial environment than the selenite ion (Howard 1977).

Data from laboratory sorption experiments.

Because selenium occurs as anionic species in the surficial environment, its adsorption behavior is controlled primarily by surface-complexation reactions on oxide minerals including iron oxides and oxyhydroxides (Balistrieri and Chao 1987), manganese oxides and oxyhydroxides, clays (Bar-Yosef and Meek 1987), and other minerals with affinities for anionic species. These surface-complexation reactions are quite sensitive to pH. For example, adsorption on iron oxyhydroxides decreases for both selenite and selenate ions with increasing pH (Balistrieri and Chao 1987).

Selenate ions appear to sorb dominantly in the outer layer of the electrical double layer present on oxide surfaces, whereas selenite tends to sorb in the inner layer (Hayes et al. 1987). Selenate ions are subject to ionic-strength effects as well as competitive effects with sulfate and other anions in solution, presumably because they sorb in the outer layer. Selenite ions are not subject to ionic-strength effects but may be subject to competition from other anions sorbing on inner-layer sites (Hingston et al. 1971).

Studies of selenite adsorption on soils in the pH range expected for Yucca Mountain groundwaters indicate relatively limited adsorption (< 30%) from 0.05 N chloride solutions containing 0.16 to 0.63 mg/l selenium (Neal et al. 1987). This limited sorption potential will likely be further decreased in natural waters containing high concentrations of competing anions.

Data for selenium sorption coefficients on Yucca Mountain rock samples in contact with J-13 water have been summarized by Thomas (1987). Most

measured values are less than 5 ml/g, although values up to 25 ml/g have been reported (Ogard and Kerrisk 1984; Conca and Triay 1994). Measured values do not appear to correlate with rock type. A puzzling feature of the data is that, for a given rock sample, sorption coefficients are larger in the higher pH experiments (pH of 8.8) compared to the lower pH experiments (pH of 6.0). This result is contrary to the pH dependence predicted on the basis of double-layer theories. Neal et al. (1987) noted a similar effect for selenium sorption on soils for a solution phase enriched in calcium. They suggested the effect may be due to the formation of a calcium-rich surface precipitate or, alternatively, a change in surface charge due to the adsorption of divalent calcium cations. Benjamin (1983) made similar observations involving other divalent cations. These data suggest that in groundwaters relatively enriched in calcium, and perhaps other divalent cations, selenium adsorption may be somewhat enhanced in the alkaline pH range.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

Sorption coefficients for selenium on Yucca Mountain rock samples have only been measured in J-13 water. These experiments do not show the expected decrease in sorption coefficient with pH. Therefore, variations in pH over the range expected in Yucca Mountain groundwaters do not appear to be the most important groundwater compositional parameter in the sorption behavior of this element. Based on the data obtained in other studies, divalent cations may have a significant impact on the sorption behavior of this element in Yucca Mountain rock-water systems. Additional experiments with waters enriched in divalent cations (such as UE-25 p#1 water) may be productive and may enlarge the range of selenium sorption-coefficient values appropriate for use in performance-assessment calculations.

Uranium

Behavior in solutions representative of Yucca Mountain groundwaters.

Under the redox potentials expected in Yucca

Mountain groundwaters, particularly in the unsaturated zone, uranium should be in the +6 oxidation state. In this oxidation state, uranium will be present in solution in a variety of complexes including $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{OH})_2(\text{aq})$, $\text{UO}_2(\text{CO}_3)(\text{aq})$, and other minor species. Phosphate, fluoride, or sulfate species will not be significant within the concentration ranges for these anions and the pH range expected in Yucca Mountain groundwaters. In the high-silica groundwaters of Yucca Mountain, the solubility-controlling compound for uranium should be haiweeite ($\text{Ca}(\text{UO}_2)_2(\text{SiO}_2)_6(\text{H}_2\text{O})_5$), according to available thermodynamic data (Bruton 1990). Interestingly, leaching experiments on uranium-oxide pellets (Bates et al. 1990) at 90°C using J-13 water produced a variety of phases on reacted surfaces that did not include haiweeite.

Qualitative evidence for behavior in the surficial environment.

Data on the behavior of uranium in the surficial environment are available from various sources. Several types of uranium ore deposits have been studied as natural analogs to repository settings. Other sources of data include studies of uranium mill-tailings piles, waste-stream outfalls, and other uranium ore deposits. Only the natural analog studies will be discussed in this section.

The deposits that have been studied as natural analogs include the deposits at Oklo, Gabon, the Alligator Rivers region in Australia, Cigar Lake in Canada, Poços de Caldas in Brazil, and Peña Blanca in Mexico. Each of these deposits has been studied in considerable detail to define the geochemical behavior of uranium and its daughter products in the environments in which the ore deposits are found. Although none of the environments are completely analogous to the Yucca Mountain site, the Peña Blanca deposit is at least situated in Tertiary volcanic tuffs similar to those present at Yucca Mountain.

A critical aspect of any analog to potential uranium migration at the Yucca Mountain site is that the

uranium source must be subject to redox potentials similar to those expected at Yucca Mountain, particularly in the unsaturated zone. This fact eliminates from detailed consideration data from the Cigar Lake and probably the Oklo deposits (Goodwin et al. 1989; Cramer and Sargent 1994; Brookins 1983).

The Alligator Rivers deposits are exposed to oxidizing conditions in a surficial environment (Gilbin and Snelling 1983). Uranium isotope-disequilibrium studies at this site indicate that uranium migration has occurred relatively recently (Snelling and Dickson 1979). However, evidence for recent transport does not by itself provide an estimate of the rate of transport and, more importantly, of the chemical controls on this rate. The latter type of information could be very useful to the Yucca Mountain Program.

At the Koongarra deposit, uranium migration is significantly retarded by the precipitation of uranyl phosphate minerals (Snelling 1980). Although phosphate concentrations in local groundwaters are not high (0.01–0.1 mg/l), significant phosphate concentrations are found in the country rocks in minerals such as apatite. The phosphate in the rocks is apparently redistributed locally by groundwater, resulting in the precipitation of uranyl phosphate minerals within the zone of weathering (Snelling 1980). This retardation mechanism is not expected to be important at Yucca Mountain, given the low phosphate concentrations found in Yucca Mountain rock units (Broxton et al. 1986).

Uranium in the zone of weathering at Alligator Rivers also appears to be associated with and is probably retarded by ferric-iron compounds (Payne et al. 1991 and others). Sorption experiments have been carried out involving uranium sorption on whole-rock samples and on pure mineral samples (Payne et al. 1991). The results of these experiments suggest that ferric hydroxides are strong sorbers of uranium in this system over a pH range of 5 to 9. This result is not particularly new as similar results on ferric oxyhydroxides have been reported

by others (for example, Hsi and Langmuir 1985). A potentially important result from these studies would be the derivation of some defensible estimate of the rate of transport of uranium in this system using the experimentally derived chemical constraints on uranium adsorption behavior and a valid groundwater flow model. Unfortunately, hydrologists who are knowledgeable about the site suggest the complicated nature of the flow system may preclude the development of defensible flow models (S. N. Davis, cited in Curtis and Fabryka-Martin 1988).

The Peña Blanca uranium deposits in Mexico provide a potentially more appropriate analog site in relation to Yucca Mountain. The primary uranium deposits at this site are hydrothermal in origin and were emplaced in structural features associated with Tertiary silicic volcanic tuffs that overlie Mesozoic calcareous basement (George-Aniel et al. 1991). In addition to the hydrothermal deposits, which contain sulfide minerals as well as uranium oxides, supergene deposits have formed locally through the leaching of uranium from the volcanic rocks and subsequent precipitation as uranyl silicate minerals, including uranophane (Murphy 1992). The supergene deposits are hosted by kaolinitized and silicified rhyolite and do not appear to contain sulfide minerals. The absence of sulfide minerals is important because sulfides, such as pyrite, oxidize readily in the surficial environment to produce acidic conditions unlike those expected within Yucca Mountain. The supergene deposits are thought to have formed in the surficial environment (George-Aniel et al. 1991), and their study may offer useful insight into the potential for migration of uranium from the proposed repository within Yucca Mountain. No data on the present-day sorption behavior or rate of migration of uranium in these deposits has been reported to date. However, several geochemical studies are currently underway to provide such data (Murphy 1992).

A qualitative study by Rosholt et al. (1971) established that uranium was leached from devitrified tuff samples but not from hydrated glassy samples

obtained from a given geologic unit. This and other data presented suggest devitrification makes the uranium in tuffs more mobile in the surficial environment. Zielinski et al. (1986) and Flexser and Wollenberg (1991) observed that uranium in Yucca Mountain devitrified tuffs was commonly associated with manganese oxides. This fact suggests that although uranium may be mobile in the unsaturated devitrified tuffs in Yucca Mountain, it could be retarded to the extent that there are manganese oxides present along the flow path with sufficient capacity to sorb the potential flux of uranium from the proposed repository horizon. Given the amount of uranium to be emplaced in the potential repository, it would seem the sorption capacity of the manganese oxides present in the mountain (Bish and Chipera 1989) would be rapidly saturated. Nonetheless, manganese oxides may significantly retard the movement of uranium in some of the fracture-flow scenarios.

Data from laboratory sorption experiments.

Data have been presented on the adsorption of uranium onto a variety of pure mineral phases in simple electrolytes. Among the solid phases investigated are goethite (for example, Hsi and Langmuir 1985), hematite (Ho and Miller 1986), silica gel (Zielinski 1980), clays (Tsunashima et al. 1981), and zeolites (Ames et al. 1983). The results reported are sometimes difficult to reconcile. For example, Hsi and Langmuir report that hematite sorbs very little of the uranium in solutions with 5×10^{-5} M uranium and 10^{-3} M total carbonate, whereas Ho and Miller report that hematite sorbs up to 100 per cent of the uranium in their experiments with similar uranium and bicarbonate solution concentrations. Both sets of experiments had similar hematite surface areas. The main difference was that the solution phase in the Hsi and Langmuir experiments also contained 0.1 M NaNO_3 . However, NaNO_3 is generally considered to be a nonreactive electrolyte, and nitrate does not form complexes with uranium in the pH range addressed in these experiments. Why there is a difference in these results is unclear. One possibility is that the surface characteristics of the solid phases used were

not the same in the two sets of experiments.

Silica gel appears to have a clear affinity for uranium as established by the results of laboratory experiments and by observations on the association of uranium with opals in nature (Zielinski 1980). According to Maya (1982), the uranium is adsorbed to silica gel as the uranyl ion, free of carbonate ligands. Zielinski has shown that sorption of uranium onto silica gel is sensitive to the total carbonate concentration of the solution phase when this concentration is above 0.01 M. Interestingly, experiments carried out at elevated temperatures (65–80°C) resulted in somewhat higher sorption coefficients. Data regarding competitive effects on silica gel between uranium and other constituents in groundwaters at near-neutral pH have not been found in the literature.

Sorption of uranium by clays has been investigated in some detail. Borovec (1981) has presented data that indicate montmorillonite has a high selectivity for uranyl ions relative to divalent ions of zinc, manganese, calcium, magnesium, cobalt, cadmium, and nickel at a pH of 6 in chloride solutions. However, Tsunashima et al. (1981) found montmorillonite has a greater selectivity for calcium, magnesium, and barium ions than for uranyl ions in nitrate solutions over the pH range from 4.0 to 4.5. Montmorillonite was found to have a greater selectivity for the uranyl ion than for sodium and potassium ions in the same solutions. Ames et al. (1983) found that uranium was strongly sorbed to montmorillonite from 0.01 M NaCl solutions but weakly sorbed from 0.01 M NaHCO₃ solutions in the pH range from 8 to 9.

Because groundwaters in Yucca Mountain contain significant concentrations of bicarbonate, calcium, and magnesium ions, these data suggest overall that uranyl ions may not compete favorably for exchange sites on clay minerals in Yucca Mountain, although quantitative prediction of the extent of exchange would require more detailed analysis.

Data available on uranium sorption on zeolitic minerals are very limited. Ames et al. (1983) report that clinoptilolite has a low affinity for trace levels of uranium in the pH range from 8 to 9 in 0.01 M NaHCO₃. Doi et al. (1975) found that uranium at concentrations of 1.0×10^{-6} g per g of solution was strongly sorbed onto clinoptilolite from perchlorate solutions in the pH range from 4 to 8.5.

Data on uranium sorption coefficients for Yucca Mountain rock-water systems were reported by Thomas (1987) and discussed by Meijer (1990, 1992). The affinity of the devitrified and vitric tuffs for trace levels of uranium is generally small ($K_d < 5$ mg/l) over the pH range from 6 to 9 in J-13 water. For zeolitic tuffs, the K_d is near zero at a pH of 9 but increases with decreasing pH to values of approximately 25 mg/l at a pH of 6 in J-13 water. This behavior suggests uranyl ions can exchange with the major cations in zeolites. In UE-25 p#1 water, uranium batch-sorption experiments were only carried out in the pH range from 8.3 to 9.3 with the result that the measured sorption coefficients were small (0–2.7 mg/l; Thomas 1988). The devitrified sample showed the largest sorption coefficient. In the pH range from 6 to 8, it is expected that the sorption coefficients for uranium in UE-25 p#1 water will increase with decreasing pH, but they will likely be smaller than the coefficients obtained for the same rock samples in J-13 water over this pH range. In H-3 groundwater, sorption coefficients were also low for zeolitic and devitrified rock types over the pH range from 9.2 to 9.3, presumably reflecting the elevated carbonate content of this water. However, data for a vitric sample showed values of 6.2 mg/l for the uranium sorption coefficient at a pH of 9. This relatively high value has not been explained.

We studied the sorption of U(VI) onto samples of the three types of tuff in J-13 water (under oxidizing conditions) at the two pH values (7 and 8.5). However, to identify the sorbing minerals in the tuffs, we also studied sorption onto the pure minerals hematite, clinoptilolite, albite, and quartz. We

found that uranium in J-13 water does not sorb onto devitrified and vitric tuffs, albite, and quartz (Table 18).

We used wet-sieved tuffs, albite, and quartz samples with particle sizes in the range from 75 to 500 μm . Initial uranium concentrations ranged from 8×10^{-8} to 1×10^{-4} M. The pretreatment period was 2 to 4 days, and the sorption period, 3 to 4 days. The negative values reported in Table 18 are the result of analytical error for the case of very little sorption (that is, a small number obtained as the difference of two large numbers). For the experimental conditions cited, uranium sorption onto zeolitic tuffs and clinoptilolite is nonlinear and can be fitted with Freundlich and Langmuir isotherms (Figs. 65 and 66).

For the clinoptilolite-rich zeolitic tuff sample G4-1510, the scatter in the data makes it impossible to conclude whether there is a significant difference between the experiments performed under a carbon-dioxide overpressure and a pH of 7 or at atmospheric conditions and a pH of 8.5 (Fig. 65). However, the experiments with pure clinoptilolite indicate that sorption increases with decreasing pH for U(VI) (Fig. 66), as is the case for Np(V). Because the major constituent of tuff sample G4-1510 is clinoptilolite, predictions of the K_a (K_d divided by the solid-phase surface area) were made for uranium sorption onto this tuff by assuming that clinoptilolite is the only sorbing phase. Inspection of Table 19 indicates that reasonable predictions are obtained with this assumption for a pH of 7 but not for a pH of 8.5. In all cases, predictions based on clinoptilolite sorption are conservative.

The sorption of uranium onto pure iron oxides (such as hematite) is very large (and large uncertainties in the K_d values result from measuring the small amounts of radionuclide

Table 18. Uranium Sorption in J-13 Water under Oxidizing Conditions

Solid phase	pH	K_d (ml/g)*
G4-268, devitrified tuff	7	2×10^{-1}
	8.5	7×10^{-1}
GU3-1405, vitric tuff	7	-5×10^{-1}
	8.5	6×10^{-1}
Quartz	7	1×10^{-1}
	8.5	7×10^{-2}
Albite	7	-5×10^{-2}
	8.5	-1×10^{-1}

*The uncertainties in the data are ± 3

left in solution after sorption). Although the measured sorption of uranium onto pure hematite is very large, sorption onto devitrified tuffs, which appear to have traces of hematite ($1\% \pm 1$), is essentially zero. This result could be due to differences in the surface of pure hematite compared to hematite in tuff. It could also be due to passivation of the hematite surfaces in the tuff by elements (such as the rare earths) that have a higher affinity for hematite than uranium and, thus, occupy the sorption sites.

Conclusions regarding sorption behavior with respect to expected variations in groundwaters.

The dominant groundwater compositional controls on the sorption behavior of uranium on Yucca Mountain rock samples will likely be pH, carbonate content, and the concentrations of calcium and magnesium ions in solution. The pH and carbonate

Table 19. Prediction of Uranium Sorption on Clinoptilolite-rich G4-1510 Tuff in J-13 Water

Initial concentration (M)	pH	Measured K_a (m)	Predicted K_a (m)*
2×10^{-7} to 4×10^{-7}	7	8×10^{-7}	8×10^{-7}
	8.5	8×10^{-7}	4×10^{-7}

*Assuming clinoptilolite is the only sorbing mineral in the tuff

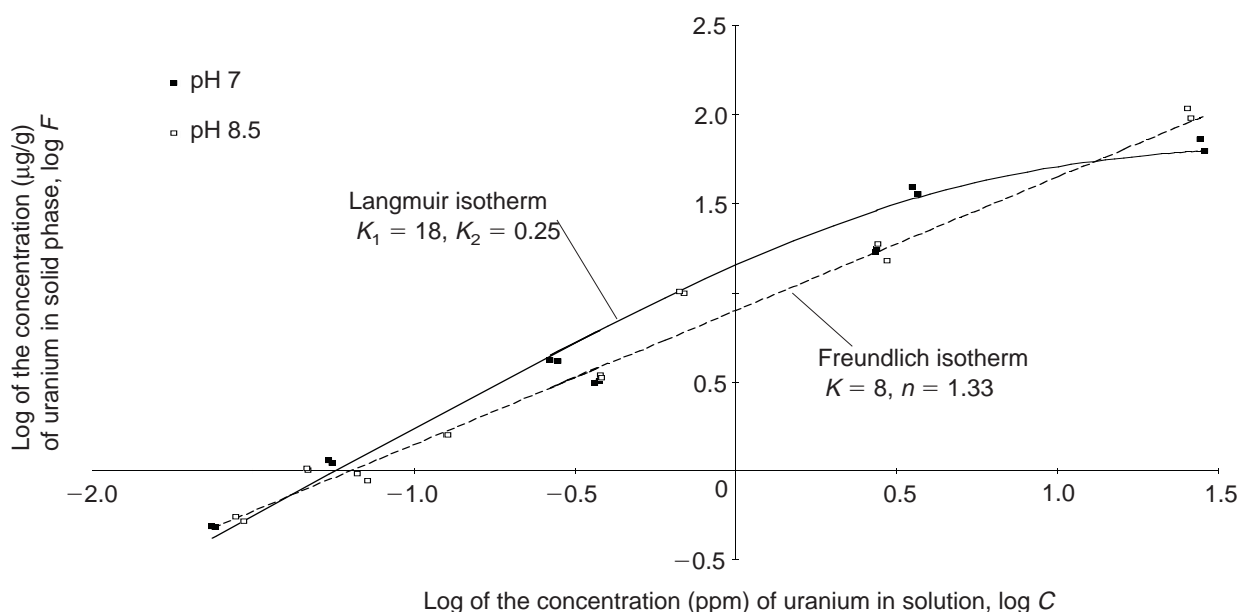


Figure 65. Uranium Sorption onto Clinoptilolite-rich Tuff. A log-log plot of the concentration of uranium in the solid phase, F , of the clinoptilolite-rich tuff G4-1510 versus the concentration of uranium in the solution phase, C , of J-13 well water. The tuff was wet-sieved to give particles that ranged in size from 75 to 500 μm . The period of pretreatment was 2 to 4 days; the period of sorption was 3 to 4 days. The data for a pH of 7 have been fitted with a Langmuir isotherm; the data for a pH of 8.5 have been fitted with a Freundlich isotherm.

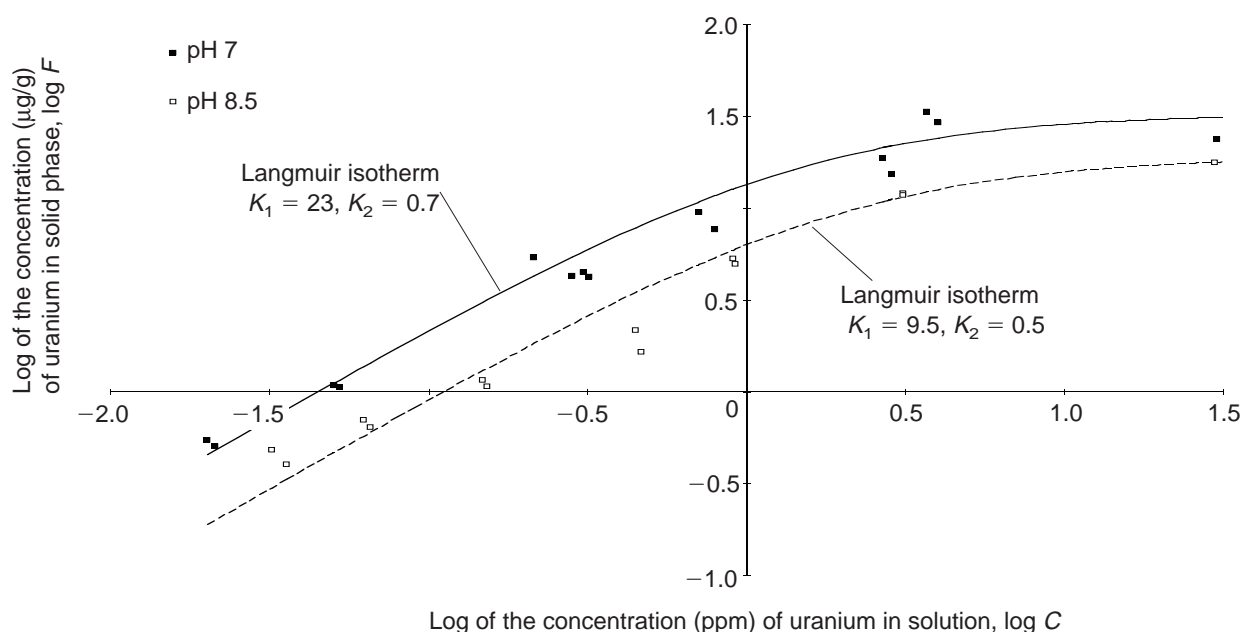


Figure 66. Uranium Sorption onto Clinoptilolite. A log-log plot of the concentration of uranium in the solid phase, F , of clinoptilolite versus the concentration of uranium in the solution phase, C , of J-13 water. The mineral was unsieved. The period of pretreatment was 2 to 4 days; the period of sorption was 3 to 4 days. The data for each pH (7 and 8.5) have been fitted with a Langmuir isotherm.

contents influence the sorption largely as a result of the decrease in carbonate complexation of uranium with decreasing pH. These two parameters are therefore not entirely independent. However, different water compositions can have different carbonate contents at a given pH. The expectation is that waters with higher carbonate contents will be associated with lower sorption coefficients. This trend would apply to both ion-exchange and surface-complexation sorption mechanisms. However, decreasing pH will have different effects on uranium sorption behavior in zeolitic and clay-rich samples versus devitrified and vitric samples. In the former samples, the uranium sorption coefficient will likely increase with decreasing pH due to the increase in uranyl ion concentrations with decreasing pH. For a given rock-water system, the magnitude of this increase will depend on the concentrations of competing ions such as calcium and magnesium in the water. For high calcium and magnesium waters, the competition effects will be substantial. Because unsaturated-zone waters are relatively enriched in calcium and magnesium, uranium sorption coefficients in the unsaturated zone may be on the low end of the range reported to date (Thomas 1987, 1988) unless the low total carbonate concentrations in these waters balance the effect of the elevated calcium and magnesium concentrations.

It will be important to carry out experiments on representative rock samples using a high-calcium-and-magnesium, low-carbonate, unsaturated-zone water composition with pH controlled over a range from 6 to 9. Similar experiments should be carried out with a high-total-carbonate and high-calcium-and-magnesium water composition, such as UE-25 p#1 water, over the pH range from 6 to 8.

Carbon, Chlorine, Iodine, and Technetium

Because carbon, chlorine, iodine, and technetium are unlikely to have significant sorption affinity in the rock-water systems expected at Yucca Mountain, their sorption behavior will not be discussed in detail. For carbon, the most robust retar-

dation mechanism will be isotopic exchange with stable carbon isotopes in groundwater and on carbonate mineral surfaces (Meijer 1993).

Chloride and iodide ions will have no significant retardation in Yucca Mountain rock-water systems and may even have slightly enhanced migration rates due to anion-exclusion effects (Ogard and Vaniman 1985). If conditions were to become sufficiently oxidizing to convert iodide to iodate, some retardation of iodine might occur in the flow system. Although such conditions might occur locally, for example, due to radiolysis effects, it is considered unlikely that such conditions would be present over a significant volume of the flow system for an extended period of time.

Technetium appears to show nonzero, although minimal, retardation in Yucca Mountain rock-water systems (Ogard and Vaniman 1985; Rundberg et al. 1985; Thomas 1988). However, the cause of this retardation has not been identified, and it may simply be an experimental artifact. Because the minimal values obtained for technetium sorption coefficients to date will not result in significant retardation of technetium, it does not seem prudent to expend funds on the detailed investigation of potential sorption mechanisms for this element. More significantly, if sufficiently reducing conditions could be shown to exist in portions of the flow system down-gradient of the proposed repository, retardation of technetium by the precipitation and sorption of Tc^{4+} species might occur.

DRAFT - 2/97